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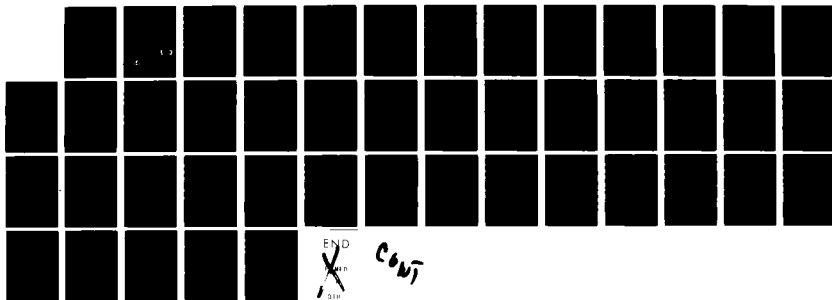
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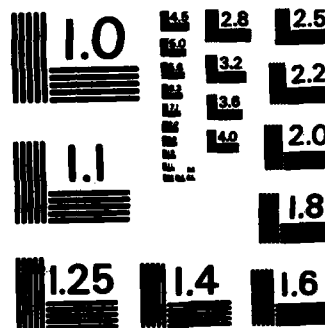
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SYNTHESIS OF ENERGETIC MATERIALS

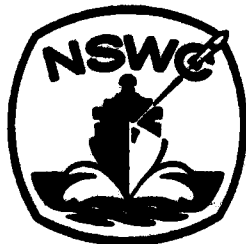
BY H. G. ADOLPH W. M. KOPPEL D. A. CICHRA M. E. SITZMANN

RESEARCH AND TECHNOLOGY DEPARTMENT

31 MARCH 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Several novel nitrodiols were synthesized and their reaction with formaldehyde to form poly- or cyclic formals was investigated. Polyformals prepared from 2,2,5,5-tetranitrohexanediol were characterized. Hexanitroperhydrodiazocine was synthesized and characterized. The synthesis of tetrazabicyclo(3.3.0)octane was initiated.		

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SYNTHESIS OF ENERGETIC MATERIALS
ANNUAL PROGRESS REPORT FOR THE OFFICE OF NAVAL RESEARCH
WORK REQUEST N000143WR20129 PROJECT RR024-02-01/02-00

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Research and Technology Department

March 1982

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FOREWORD

This report describes the synthesis of new high energy compounds and polymers performed at the Naval Surface Weapons Center in 1981 under the sponsorship of the Office of Naval Research, Code 432.



J. F. PROCTOR
By direction

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SYNTHESIS OF ENERGETIC MATERIALS

Introduction

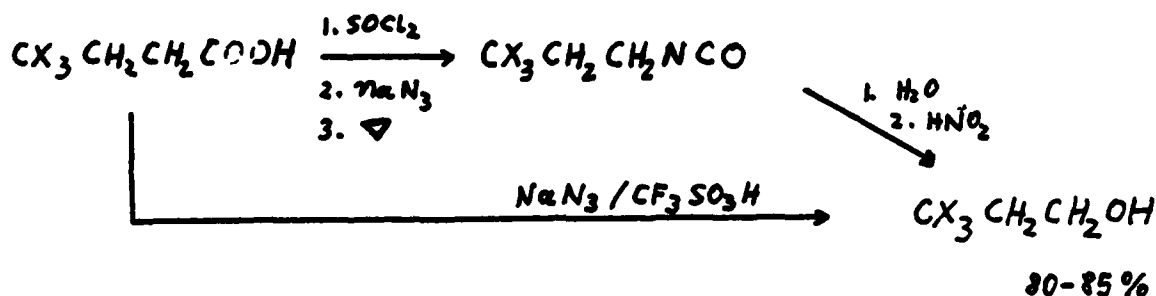
During the past year two independent efforts were pursued under this project, the synthesis of energetic monomers and polymers, and the synthesis of potentially dense cyclic and polycyclic nitramines. The former constitutes a continuation of earlier work,¹ the latter is a new start.

Energetic Monomers and Polymers

Previously under this effort¹ a systematic study of the course of formal formation between nitrodiols and formaldehyde was begun in the hope that hydroxy-terminated polyformals suitable as energetic binder components could be obtained. This work was continued during the past year and was the only topic investigated. In part this involved the synthesis of several new nitrodiols, and in part the study of their reaction with formaldehyde.

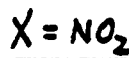
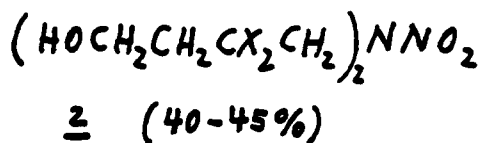
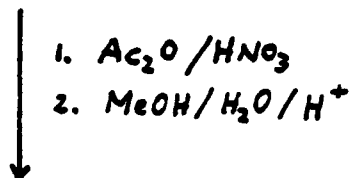
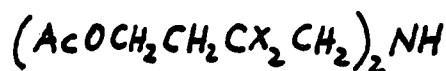
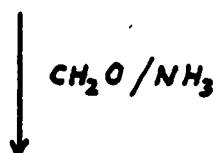
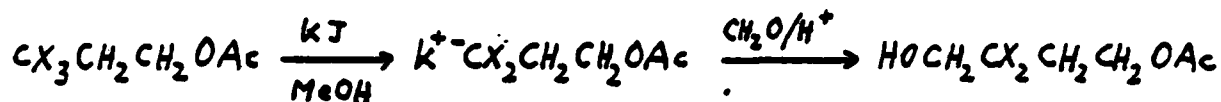
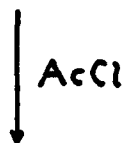
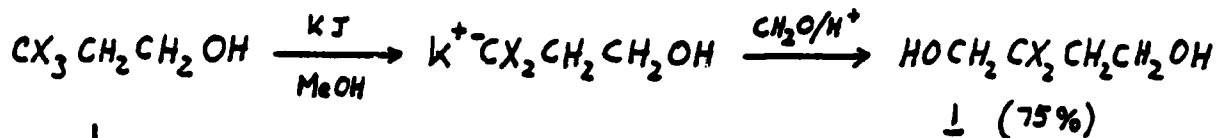
Synthesis of Nitrodiols

Additional diols were desired for continuation of the study of ring size and substituent effects on cyclic versus polyformal formation, and to obtain additional polyformals with a range of physical properties. One set of diols was obtained from 3,3,3-trinitropropanol which was synthesized for the first time during this work, although some derivatives have appeared in the literature.²



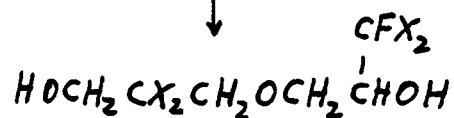
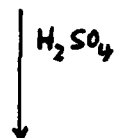
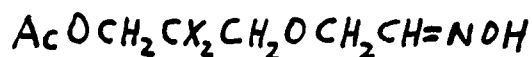
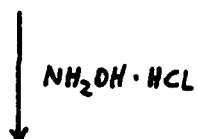
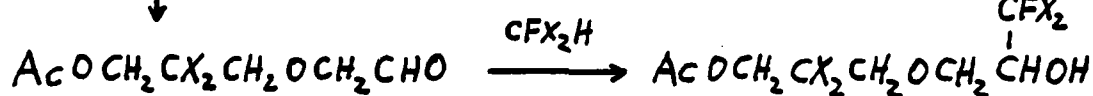
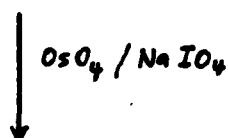
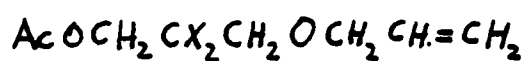
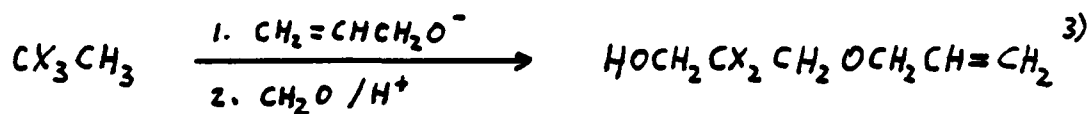
¹ H. G. Adolph, NSWC MP 81-141, "Synthesis of Energetic Monomers and Polymers," Mar 1981.

² L. T. Eremenko, "Interrelationship Between Density and Structure in an Explosive," Eleventh Symposium on Explosives and Pyrotechnics, Philadelphia, PA, Sep 1981.

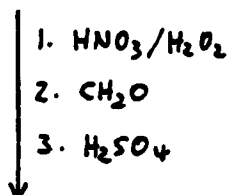


Except for the KI reductions which gave yields ranging from 65-75 percent, all steps shown proceeded in good to excellent yields so that 1 and 2 are reasonably accessible, despite the number of steps involved in the synthesis of 2. 1 had m.p. 56-58°C, that of 2 is 120-121°C.

A second set of diols (3, 4) was prepared from the monoallyl ether of A-diol as shown below:



3 (40%)

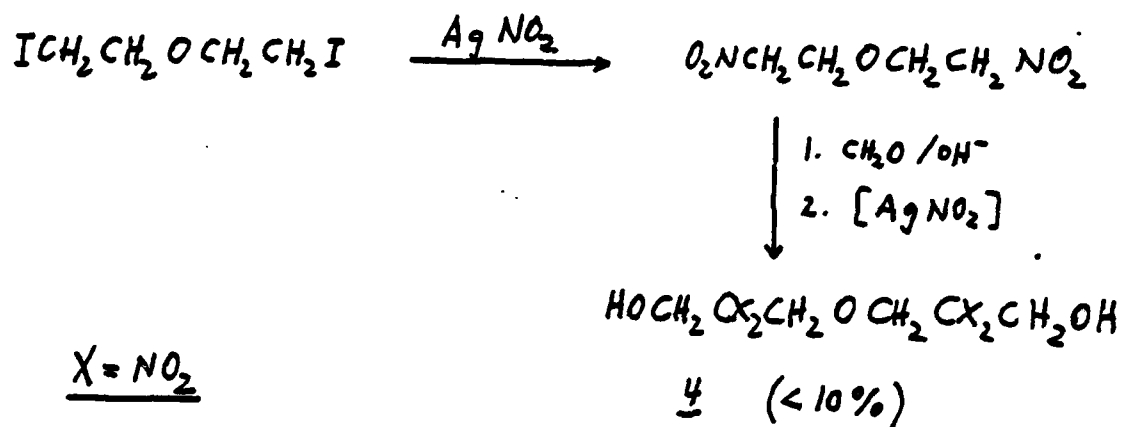


4 (15%)

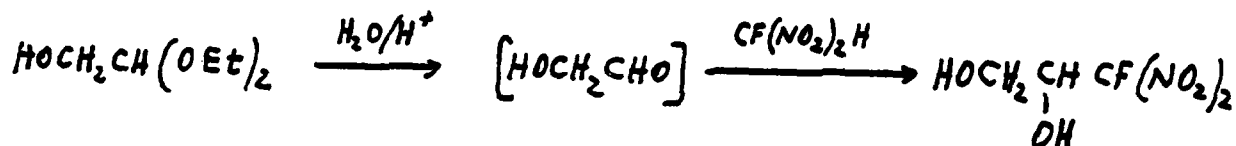
X = NO₂

³ M. B. Frankel and E. R. Wilson, J. Chem. Eng. Data **26**, 219 (1981).

Due to their difficult synthesis, 3 and 4 are currently only of interest as model compounds, even if polyformals could be prepared from them. 4 had been obtained earlier⁴ as an intermediate in the preparation of bis(fluorodinitroethyl) ether, but the isolation of pure 4 from that reaction mixture proved exceedingly difficult.



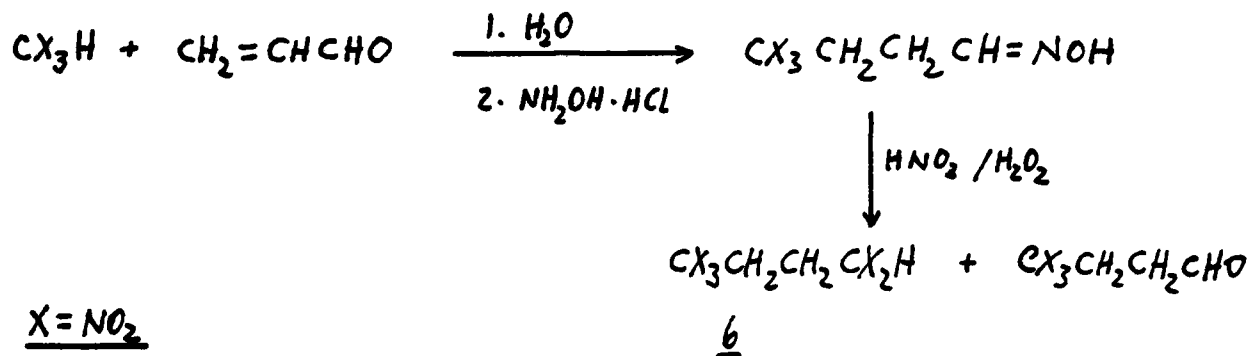
Another diol prepared by a modification of a published procedure⁵ was 3,3,3-fluorodinitropropane-1,2-diol.



Some efforts were also made to develop a better synthesis for 2,2,5,5-tetranitrohexanediol-1,6 (5) by nitration and oxidation of the readily available trinitrobutyraldoxime.

⁴ U.S. 3,531,534, "Bisfluorodinitro Ethers and Their Preparation," 29 Sep 1970.

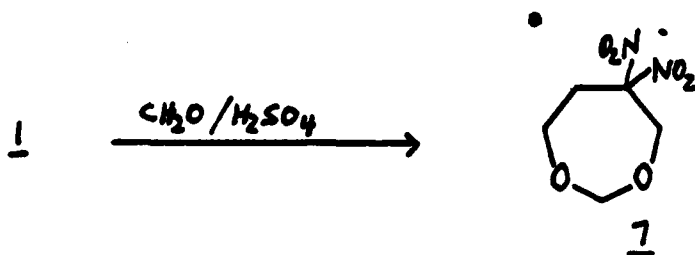
⁵ L. T. Eremenko and F. V. Oreshko, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1969, 1765.



However, a mixture of the desired 6 and starting aldehyde was obtained under all conditions tried. Further work is needed to assess the utility of this sequence for the preparation of 6 and its conversion to 5.

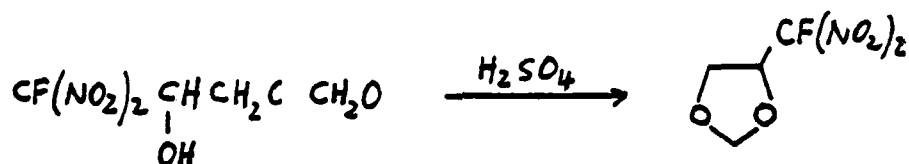
Reaction of Nitrodiols with Formaldehyde

2,2-Dinitrobutanediol-1,4 (1) reacted readily to form dinitrodioxepane in 70 percent yield (not optimized), 7. This was expected since 1,4-butanediol itself forms dioxepane in the reaction with formaldehyde and acid. The unsubstituted dioxepane can be polymerized. Polymerization of 7 has not yet been attempted. In contrast to its more symmetrical 6-membered ring analog,



5,5-dinitro-1,3-dioxane, 7 is a liquid at room temperature.

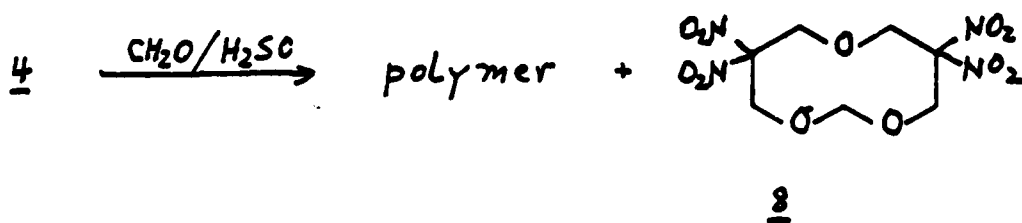
Similarly, the reaction of 3,3,3-fluorodinitropropane-1,2-diol with CH_2O /concentrated H_2SO_4 gave only the cyclic formal. No attempts have been made to polymerize it.



The reaction of ol 2 with formaldehyde is being studied at present. Results are incomplete a greater tendency for cyclic formal formation compared with diol 5 is noted.

Alcohol 3 did not as readily with formaldehyde/concentrated sulfuric acid as 1. Thus, in cent, 96 percent, and 100 percent H_2SO_4 , the major fractions isolated on up were unreacted starting material. Product fractions amounted on <25 percent yields. GPC analysis showed the products were low m.w.s containing no more than a few monomer units. It is believed that trimeric cyclic formal is one of the products but this has not been established unequivocally.

Alcohol 4 was reacted with $\text{CH}_2\text{O}/\text{H}_2\text{SO}_4$ in the presence of some sulfolane to provide a homogeneous mixture. The product obtained on work-up was found by GPC analysis consist of low molecular weight oligomers containing no more than monomer units. A small amount of solid isolated was homogeneous GPC and is probably the cyclic formal 8.



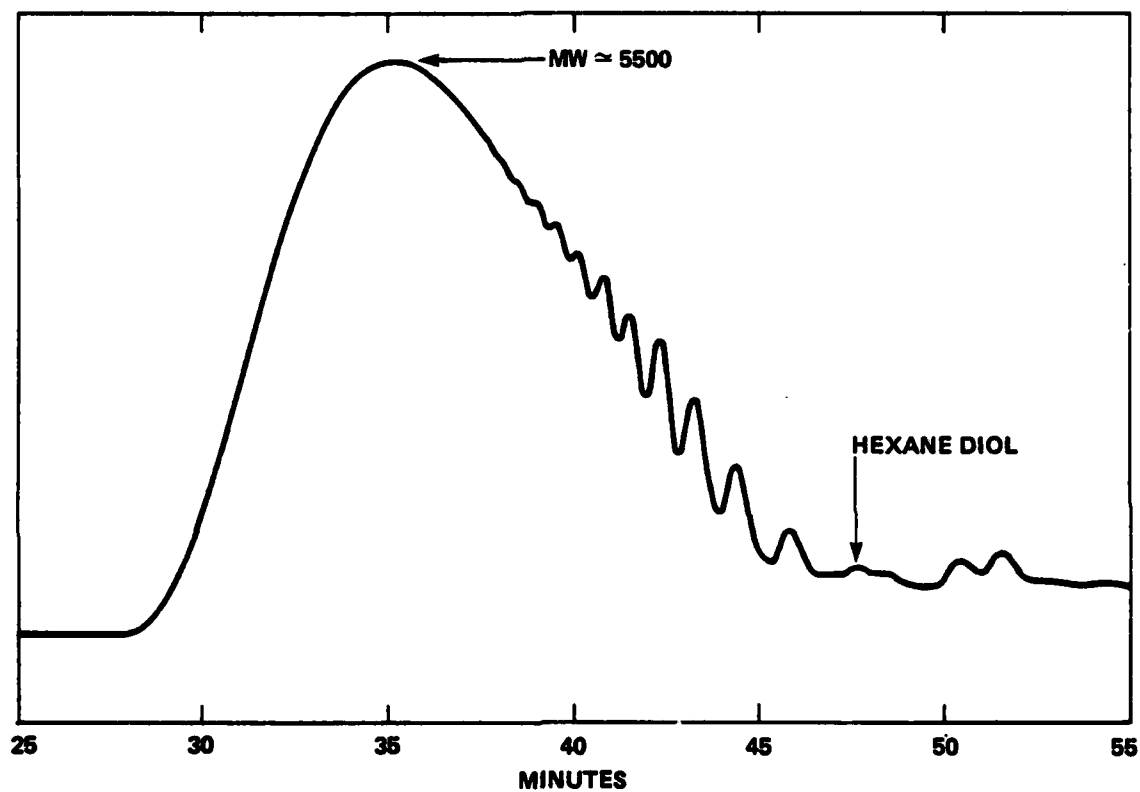


FIGURE 1. GPC CHROMATOGRAM OF A 2,2,5,5-TETRANITROHEXANE -1,6- DIOLPOLYFORMAL

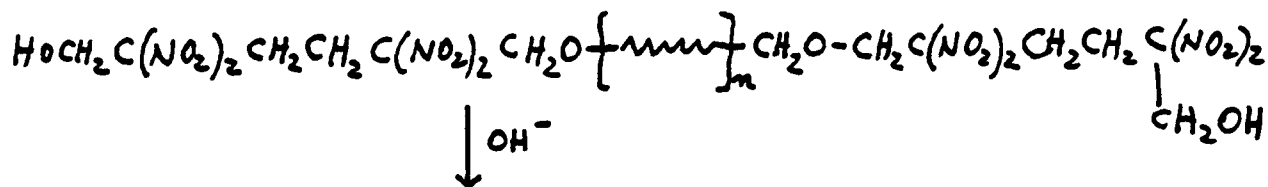
The reaction of diol 5, which had previously been found¹ to give essentially only polymer in the reaction with formaldehyde and concentrated sulfuric acid, was studied in more detail. Products were characterized by GPC analysis and the effects of varying reaction conditions on m.w. were established. Most runs were carried out in H₂SO₄/sulfolane mixture to ensure complete solution of the starting diol before addition of trioxane as a methylene chloride solution. In these runs, the diol concentration, the trioxane addition time, and the diol: formaldehyde ratio were varied to determine conditions which could give the desired low m.w. prepolymers. However, the first two parameters had little effect and the products all had m.w. peaks (GPC) near 5500. A typical chromatogram is shown in figure 1. These polymers showed some variation in melting points (from 120-135° to 145-165°) which does not appear to be related to m.w. The only effect of varying the reactant ratio was a lowering of the yield of polymer as shown in table 1, but no decrease in m.w.

TABLE 1. EFFECT OF CHANGING REACTANT RATIO ON POLYFORMAL FORMATION FROM 5

Diol CH ₂ O (Mol Ratio)	MW (Nominal)	MW (Obs., Max.)	Yield (%)
10 9	3250	5500	78
6 5	1938	5500	65
3 2	954	6500	52

When the condensation was carried out at much lower diol concentration than above, a mixture of unreacted diol and formal oligomers containing only a few diol units were formed. A polymer of somewhat lower m.w. (peak at approximately 3500) was obtained when the condensation reaction was carried out in concentrated H₂SO₄ alone but in this case an irregular and not reproducible m.w. distribution resulted (figure 2). A similar but more regular material was obtained by fractionation of the higher molecular weight product with ethyl acetate (figure 3).

An attempt was made to determine the functionality of the polymers by UV analysis. In alkaline aqueous THF solution, the polymers showed an absorption maximum at 372.5 nm as could be expected from a polymer diol of this type (the diol 5 under the same conditions has λ_{\max} 375 nm (ϵ 26,300)).



¹ H. G. Adolph, NSWC MP 81-141, "Synthesis of Energetic Monomers and Polymers," Mar 1981.

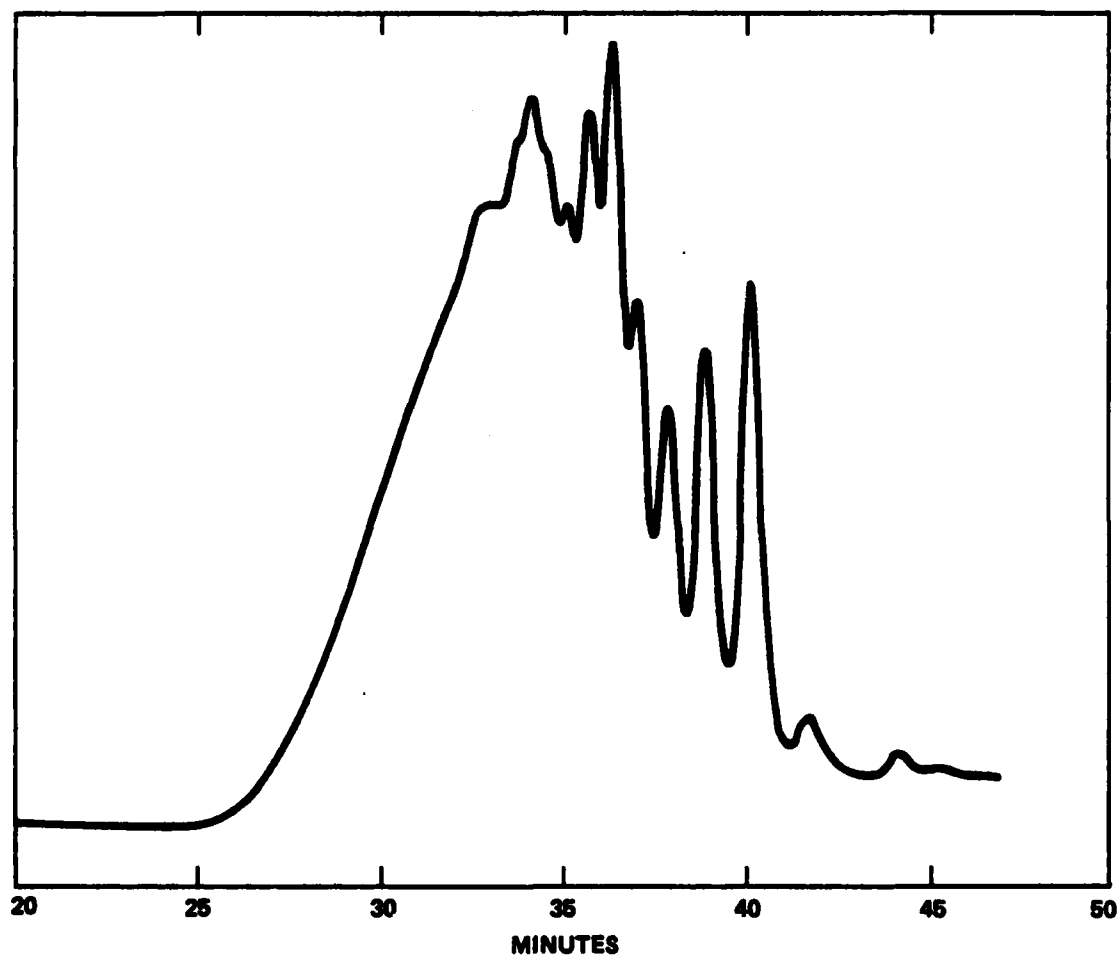


FIGURE 2. POLYFORMAL FROM REACTION IN H_2SO_4 ALONE

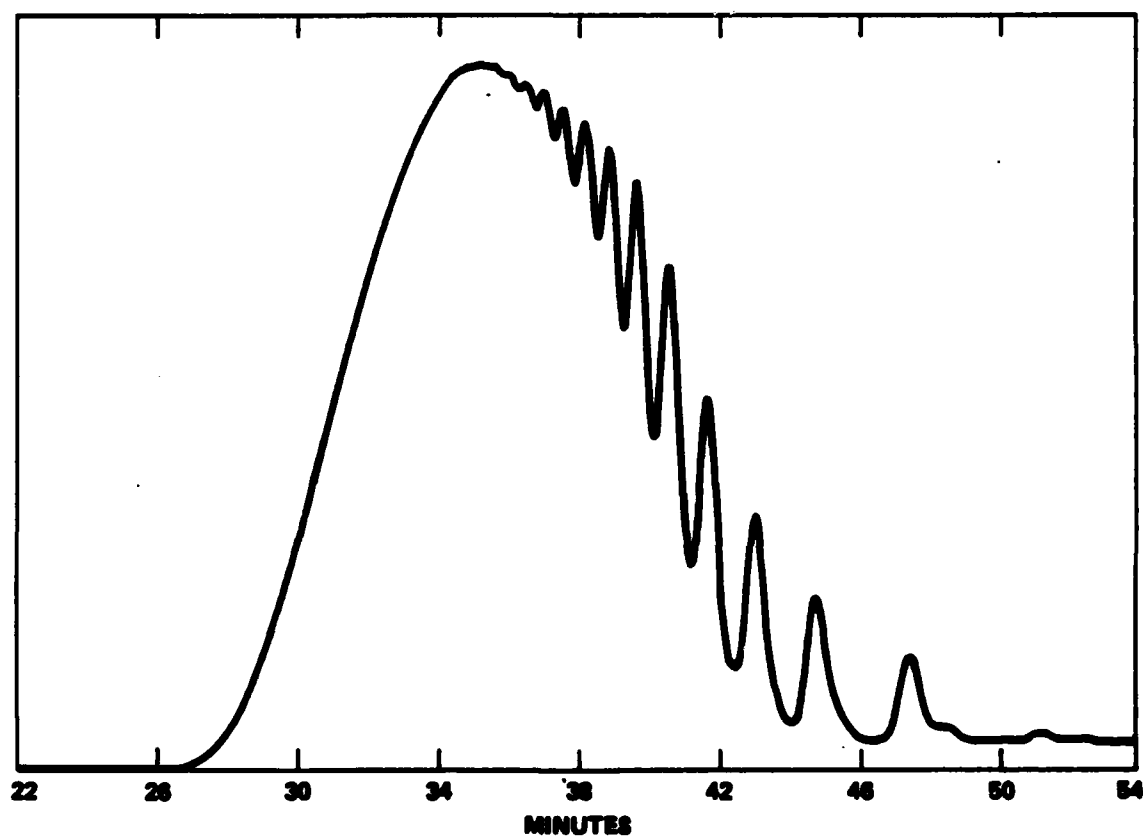
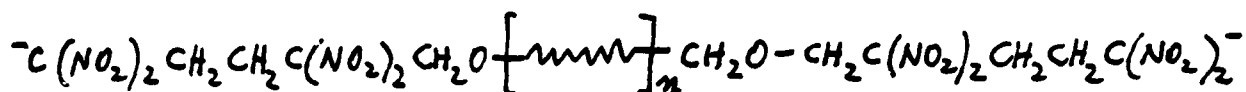


FIGURE 3. GPC OF LOW M.W. POLYFORMAL FRACTION

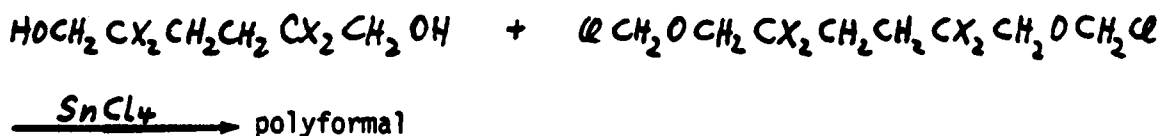


$$\lambda_{\text{MAX}}^{\text{aq. THF}} = 372.5 \text{ nm}$$

If one assumes the same molar absorptivity for the polymer as for the diol 5, then a m.w. of 2700 is calculated from the experimentally observed absorption. However, it is known that increasing separation of the negative charges in the dianion results in higher absorptivity (e.g., ϵ for DINOL is 33,000).⁶ Assuming a molar absorptivity like that of DINOL for the polymer, a m.w. of 3500 ± 100 was calculated for several of the polymer samples which had m.w. peaks near 5500 in the GPC. This can be considered good qualitative support for the assumed structure of a polyformal diol shown above.

The 5500 m.w. polymers are insoluble in CH_2Cl_2 and MeOH, but are readily soluble in ethyl acetate, acetone, acetonitrile, and THF. They are soluble in BDNPF/A nitro plasticizer, especially at elevated temperature, but the solubility in FEFO is limited. The lower m.w. fraction described above was more soluble in BDNPF/A and FEFO. The density (by flotation) of 5500 m.w. polymer is 1.57-1.58 g/cm³. The heat of formation per $-\text{CH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}-$ unit is estimated to be -140 Kcal/mol; with this and the above density, a detonation pressure of 218 Kbar and a detonation velocity of 7.30 km/sec is calculated for the uncrosslinked polymer.

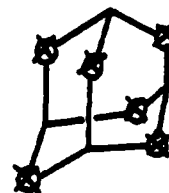
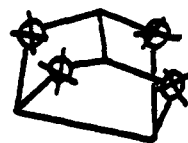
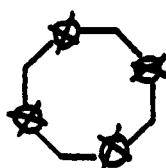
Solutions of the 5500 m.w. polymer in BDNPF/A + adiponitrile as coplasticizer were crosslinked with a HMDI/PAPI mixture and dibutyltin dilaurate catalyst. Crosslinking was successful, thus confirming the assumed diol structure of the polymer, but the low solubility of the polymer in the plasticizer carried over into the cross-linked material and gave rise to plasticizer exudation from the cured product. It is hoped that this problem will be solved by the use of a lower m.w. prepolymer, and efforts to prepare these will be continued using other methods for the preparation of the polyformal such as reaction of diol 5 with the bis(chloromethyl) ether derived from it:



⁶ T. N. Hall and K. G. Shipp, NOLTR 61-6, "Preparation and Properties of 2,2,8,8-Tetranitro-4,6-dioxo-1,9-nonanediol, DINOL," 21 Mar 1961.

Potentially Dense Nitramines

Holden's method for calculating crystal densities⁷ is based on a sufficiently large data base to convey some significance to differences between calculated and observed densities. On this basis features of molecular structure can be identified which are often found in "exceptionally dense" compounds and thus may be responsible for exceptional crystal density. Such features were found to include the nitramine and bis(2,2-dinitroethyl) nitramine moieties and polycyclic ring structures. This led to a series of target structures for our synthesis effort of new high density compounds which are summarized by the general structures shown below:



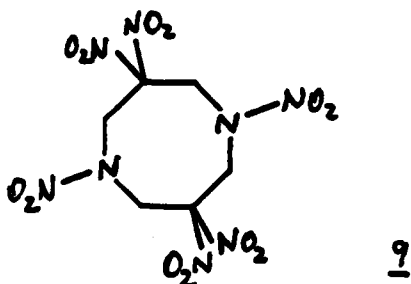
⁷ D. A. Cichra, J. R. Holden, and C. Dickinson, "Estimation of 'Normal' Densities of Explosive Compounds from Empirical Atomic Volumes," NSWC TR 79-273, 19 Feb 1980.

We envisioned that some of these structures might be accessible via the Mannich reaction of suitable dinitroalkanes, formaldehyde and other aldehydes, and ammonia as an amine:



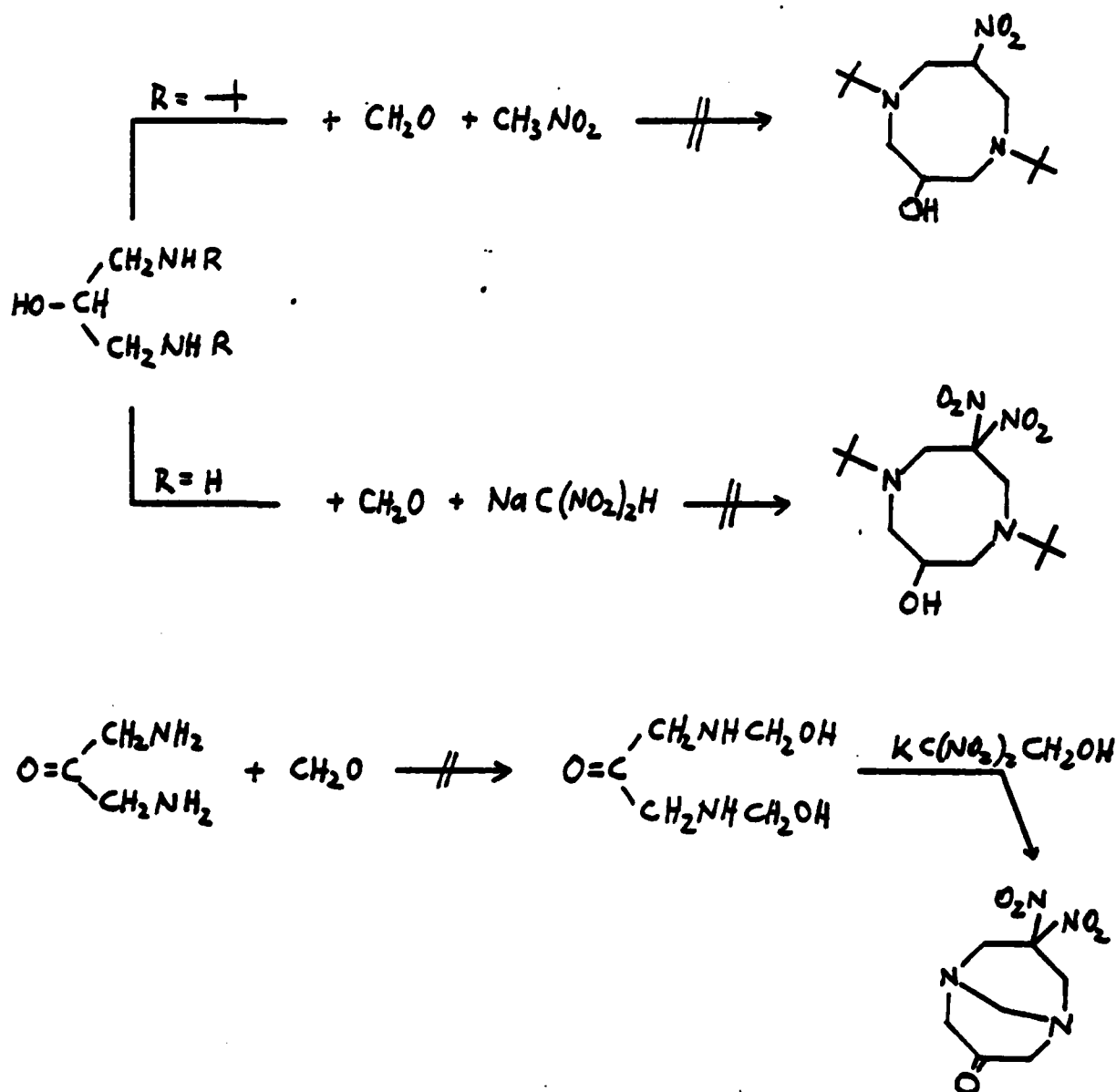
Since the eventual objective was a nitramine, methods for nitrolysis of the N-R'' or N-R''' linkages would be needed in those cases where R'' or R''' could not be H but needed to be alkyl groups for synthetic reasons. A literature search indicated that only sketchy information was available on the subject. A study of the nitrolysis of tertiary amines was therefore undertaken with the t-butyl group being R'' or R'''.⁸ This study was completed during the past year and is described in the appendix in a manuscript accepted for publication in the Journal of Organic Chemistry.

Our initial synthetic efforts centered on the HMX analog 9 which has a higher oxygen content than HMX and should be a valuable explosive and propellant ingredient if its density were equal to or greater than that of HMX.⁸

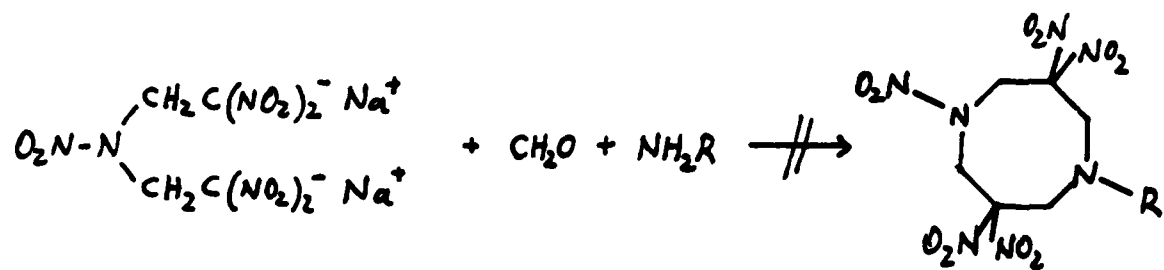


A variety of approaches were tried, initially with little success. These are summarized in the following equations:

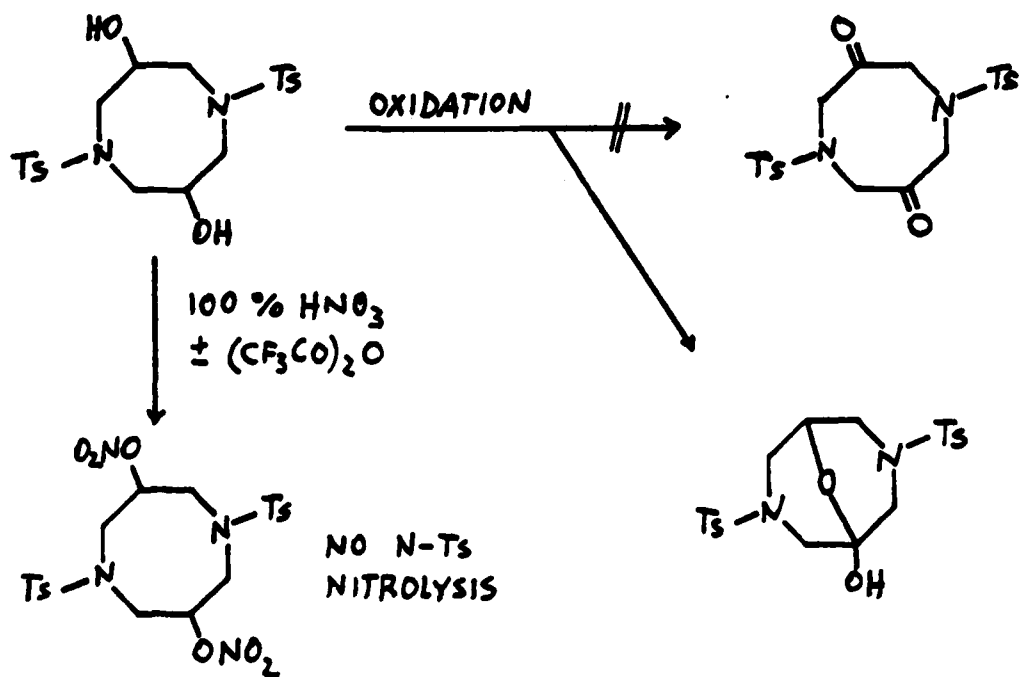
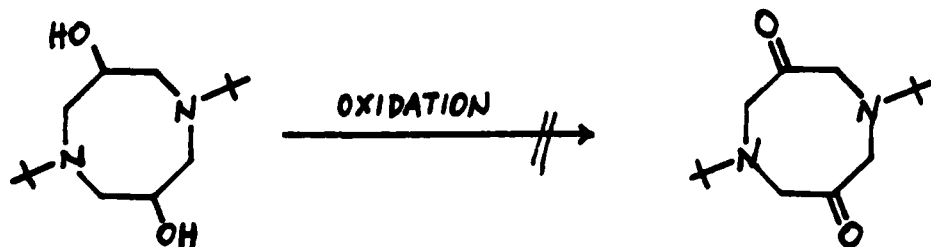
⁸ This work was also sponsored by U.S. ARADCOM, Dover.



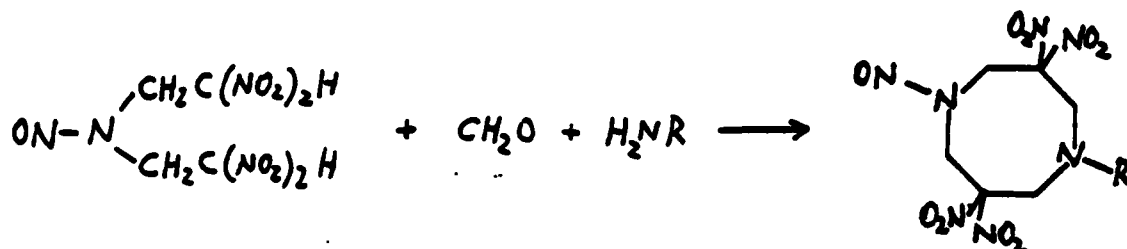
The latter sequence has been reported in a Chinese abstract submitted to the American Chemical Society with no experimental details, but in our efforts so far the reaction did not work.



R = H, Me, t-Butyl



While we were unable to effect the Mannich condensation of bis(2,2-dinitro-ethyl)nitramine or its sodium salt with formaldehyde and amines, a recent Russian paper⁹ indicated that such condensations are successful with the corresponding nitrosamine. Based on this observation we were able to prepare several potential precursors, 10 a-c, to the target compound 9.

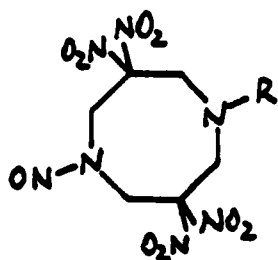


10 a : R = Me ; 85%

b : R = CH(CH₃)₂ ; 47%

c : R = H ; 81%

Several unsuccessful attempts were made to nitrolize 10a and b as well as the corresponding nitramines directly to 9; these are summarized in the following equations. In most cases the starting material was consumed but the desired product was not formed.



R = Me, i-Propyl

a) AcOH/NaNO₂

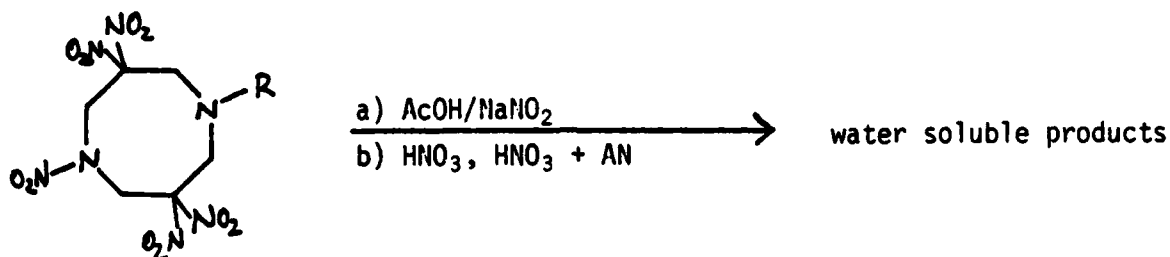
b) 100% HNO₃ + AN or AcOH/HCl

c) 90% HNO₃ (R=i-propyl)

a) 40% starting material

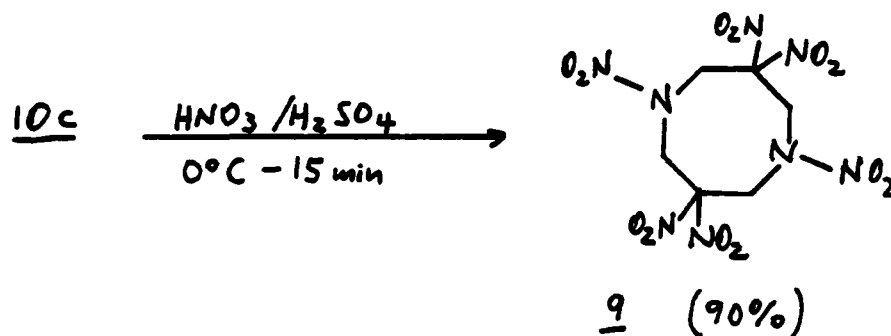
b,c) water soluble or intractable products

⁹ L. T. Eremenko, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1981, 1676.



$R = \text{Me}, i\text{-Propyl}$

10c on the other hand could be converted readily to 9 by treatment with mixed acid.

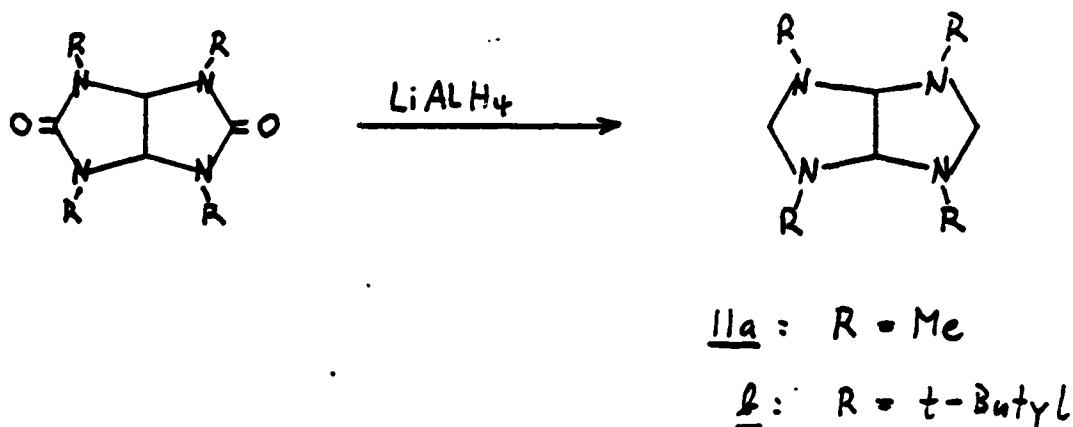


9 has the following properties:

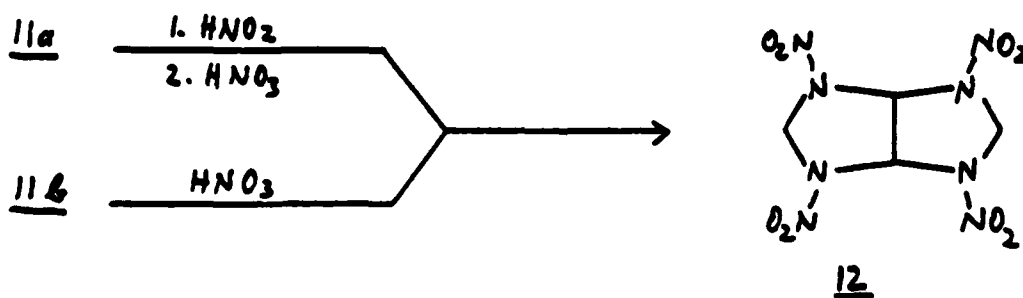
M.P. approximately 250°C (dec.)
 $\rho_o = 1.864 \text{ g/cm}^3$ (x-ray diffraction)
 I.S. = 21.4 cm (HMX = 23.6 cm)
 $\Delta H_f = -33 \text{ Kcal/mol}$ (estimated)
 DSC = onset, 500°K (HMX, 550°K)

Because of the lower density and more negative ΔH_f , 9 is not as good an explosive as HMX. The calculated detonation pressure is 358 Kbar, about halfway between RDX and HMX (342 and 382 Kbar, respectively). However, the compound may be of interest as a propellant ingredient if, as is likely, it has different burning characteristics (rate, slope) from HMX.

Another effort which we initiated during the past year is the synthesis of dehydro-HMX, 12, via nitrolysis of tetraalkyl precursors 11 a, b:

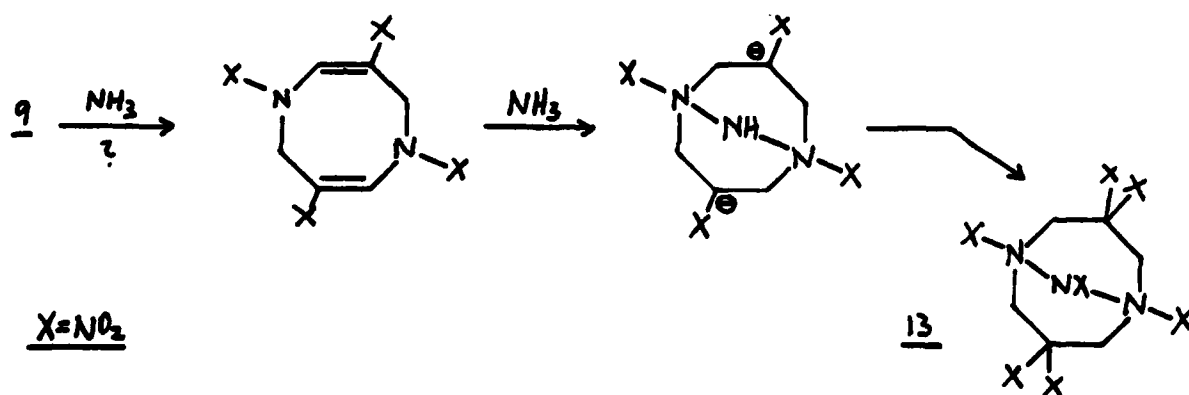


11a has been synthesized using a published procedure.¹⁰ The synthesis of 11b is underway. Applying the methods identified in our nitrolysis study, the nitrolysis of 11a and the nitrolysis of 11b should lead to 12:

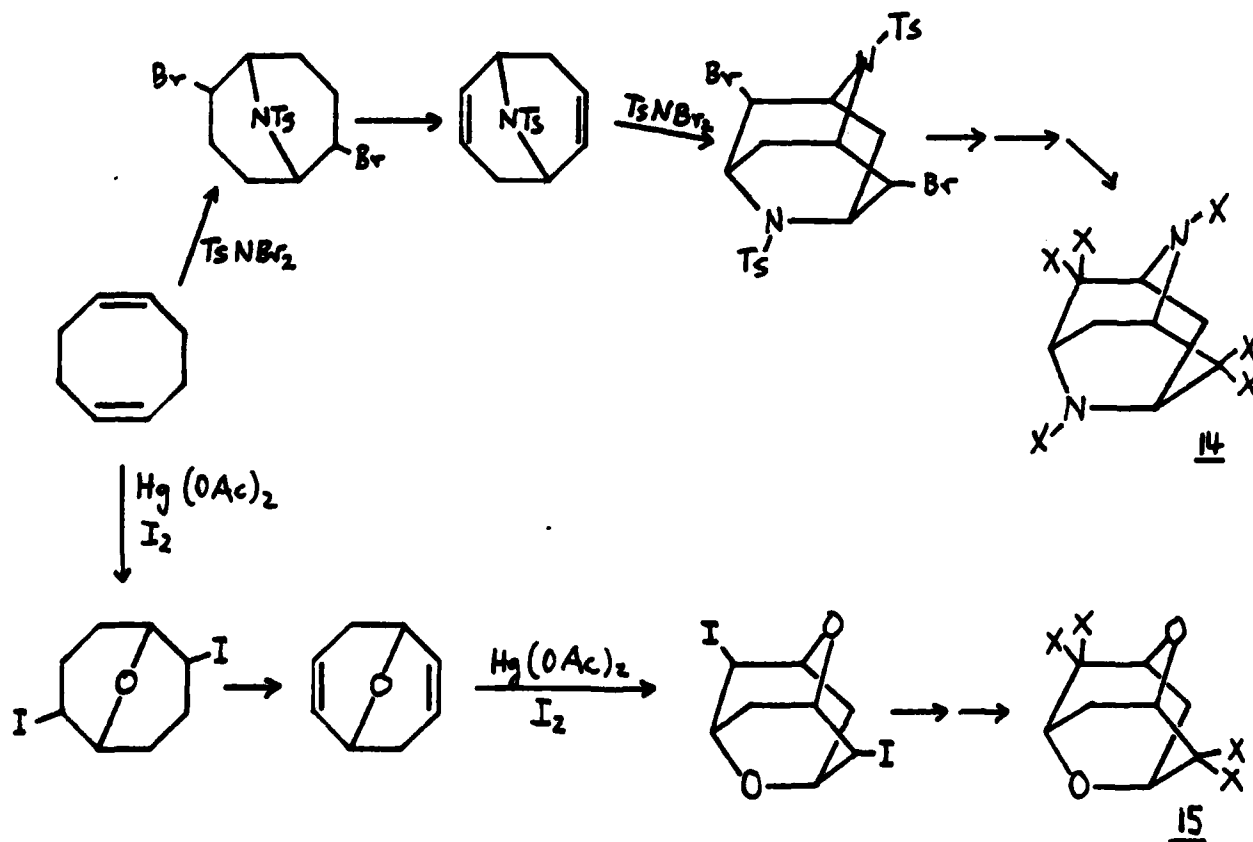


¹⁰ S. F. Nelsen and P. J. Hintz, J. Amer. Chem. Soc. 94, 7114 (1972).

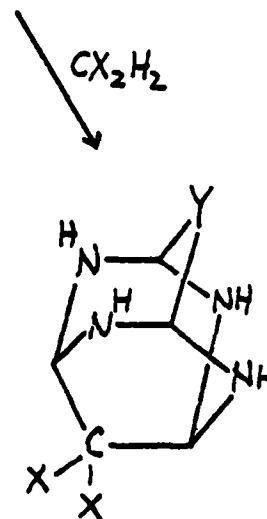
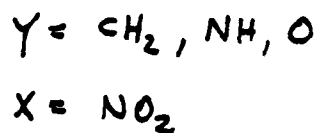
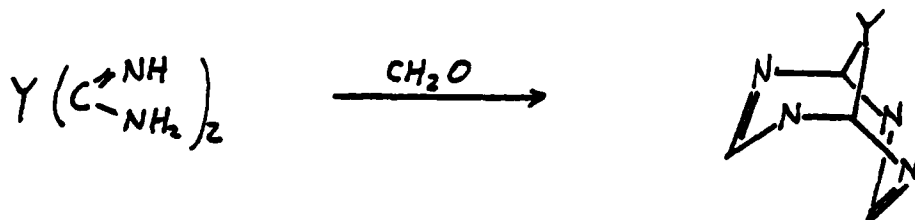
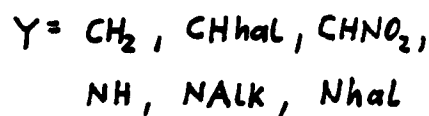
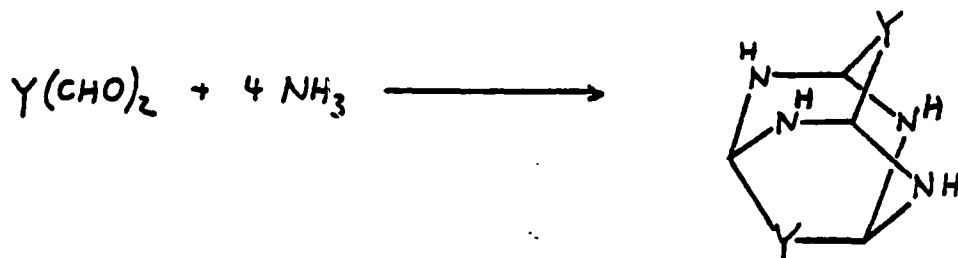
In future work the nitro-nitroso and dinitroso analogs of 9 will be prepared by nitrosation and nitration of 10c. Also, elimination-addition reactions with 9 will be investigated as a potential approach to a heptanitro-bicyclononanone (13).



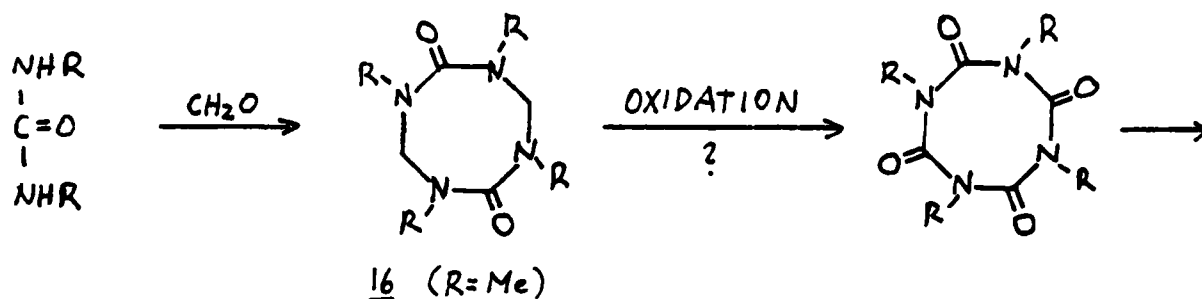
The synthesis of dihalo-dioxa- and diazaadamantanes and their conversion to the corresponding hexa- and tetranitro compounds, 14 and 15, will be initiated.



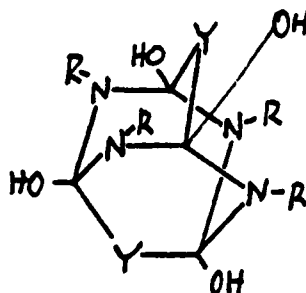
We also plan to look at condensation reactions of 1,3-dicarbonyl compounds and their aza analogs as an approach to the synthesis of tetra-, penta-, and hexaazaadamantanes:



In analogy to the known synthesis of the tetramethyl dioxotetrazocine, 16, the corresponding tetra-*t*-butyl compound will be prepared as a possible precursor for some different types of energetic adamantanes:



transannular
addition of
NH₃ or OH₂



Y = NH, O

R = Me, t-butyl

then nitrolysis of R;
nitration of OH and NH

Experimental

See reference 11 for precautions in working with fluorodinitromethane and other fluorodinitro compounds. Melting points are uncorrected. Microanalyses are by Galbraith Laboratories, Knoxville, Tennessee. Nmr spectra were obtained on a Varian E1-390 spectrometer. Chemical shifts are in ppm relative to TMS as internal standard. Temperatures are in °C unless otherwise noted.

3,3,3-Trinitropropanol. 4,4,4-Trinitrobutyric acid (210 g, 0.94 mol) was added to 534 ml (908 g) of trifluoromethanesulfonic acid stirred in a 2000 ml, 3-neck, round-bottom flask. The solution was heated to 60° (oil bath) and sodium azide (100 g, 1.54 mol) was added in approximately 2 g portions over a six hour period. (A stream of nitrogen was kept flowing over the reaction mixture during the addition to dilute and expel excess HN₃.) Stirring was stopped and the thick mixture was heated overnight at 50° before it was poured onto ice to give an aqueous solution (2500 ml) which was extracted with 3x300 ml of methylene chloride. Two grams of unreacted trinitrobutyric acid were recovered from the CH₂Cl₂ extracts. The aqueous solution was cooled at 10-14° while a solution of 140 g of sodium hydroxide in 200 ml of water was added dropwise with good

¹¹ H. G. Adolph, J. Org. Chem. **35**, 3188 (1970).

stirring. The solution was then heated to 35° before a solution of 121 g (1.75 mol) of sodium nitrite in 400 ml of water was added over a 30 minute period. (Some cooling was necessary to maintain the temperature at approximately 40° during the addition.) The solution was heated at 60° for one and a half hours before it was cooled to 25° and extracted with 2x500 ml methylene chloride. It was then saturated with sodium chloride and extracted with 3x500 ml CH₂Cl₂. The combined extracts contained 161 g (87.7 percent) of crude trinitropropanol.

The alcohol was used without purification for subsequent reactions. A pure sample (mp 24-25°C) of it as well as of the major impurity (mp 88-89°C dec.) was obtained by chromatography on Silica Gel 60 (EM Reagents). The nature of the by-product was not established; the Nmr and IR spectra indicate that it is not a trinitromethyl compound. The trinitropropanol gave the following results -- ¹H Nmr (CDCl₃): δ 1.87 (t, 1H), 3.30 (t, 2H), 4.10 (double t, 2H). Mass spectrum m/e (relative intensity) 196 (M+1, 7), 178 (M-16, 100). Analysis calculated for C₃H₅N₃O₇: C, 18.47; H, 2.58; N, 21.54. Found: C, 18.40; H, 2.62; N, 19.72.

Potassium 2,2-Dinitropropanol. To a stirred solution of 32.0 g (0.164 mol) of crude 3,3,3-trinitropropanol in 460 ml of methanol was added 68 g (0.41 mol) of potassium iodide. The mixture was stirred at ambient temperature for five days before the yellow precipitate was removed by filtration and washed with methanol. The yellow salt was added to 150 ml of methanol and the mixture was stirred at room temperature for a short time before it was cooled in ice. Filtration gave 19.6 g (64 percent) of yellow salt. Upon further standing the reaction solution gave an additional 5.6 g of product raising the total yield to 25.2 g (82 percent). ¹H Nmr (D₂O, TMS capillary): δ 3.33 (t, 2H), 4.20 (t, 2H).

2,2-ditrobutane-1,4-diol (1). To a solution of 19.6 g of potassium 3,3-dinitropropanol stirred at ambient temperature was added 20 ml of 36 percent formalin solution followed by the addition of 11 ml of concentrated hydrochloric acid over a three minute period. A small amount of precipitated iodine was removed by filtration and the filtrate (adjusted to pH 4) was allowed to stand for five hours before it was extracted with 3x90 ml of ether. Removal of the ether gave 15.3 g of a solid (mp 47-55°) which was stirred with 80 ml of chloroform at ambient temperature to give 13.4 g (72 percent) of white solid, mp 55-57°. Crystallization from methylene chloride gave 12.2 g, mp 56-58°. ¹H Nmr (CD₂Cl₂): δ 4.65 (d, 2H), 2.95 (m, 2H), 3.35 (t, 1H), 2.92 (t, 2H), 2.12 (t, 1H).

Analysis calculated for C₄H₈N₂O₆: C, 26.67; H, 4.48; N, 15.15. Found: C, 26.62; H, 4.51; N, 15.42.

3,3,3-Trinitropropyl Acetate. Acetyl chloride (125 ml) was added to a dried (MgSO₄) solution of 150 g of crude trinitropropanol as prepared above and cooled in an icebath. The solution was slowly warmed to reflux temperature and held overnight. The reaction solution was concentrated to 800 ml by distillation before it was cooled and poured onto ice water. The mixture was stirred for 30 minutes before the CH₂Cl₂ layer was separated, dried over MgSO₄, and the solvent removed to give 183 g (100 percent) of crude trinitropropyl acetate as a light green solid.

A similar reaction employing 31.9 g of crude trinitropropanol, 50 ml of methylene chloride and 25 ml of acetyl chloride gave, after addition of hexane to the CH_2Cl_2 solution and chilling, filtering off the solid, concentrating and chilling again, 34.5 g (88.9 percent) trinitropropyl acetate. A second recrystallization from CH_2Cl_2 /hexane gave material of mp 47-49°C; ^1H NMR (CDCl_3): δ 2.06 (s, 3H), 3.45 (t, 2H), 4.55 (t, 2H).

Analysis calculated for $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$: C, 25.32; H, 2.98; N, 17.72. Found: C, 25.31; H, 3.01; N, 17.27.

Potassium 3,3-dinitropropyl acetate. Potassium iodide (338 g, 2.03 mol) was added to 183 g (0.77 mol) of crude 3,3,3-trinitropropyl acetate in 2100 ml of methanol. The mixture was stirred at 40° for 24 hours before it was cooled to 20° and the yellow salt removed by filtration. The product was stirred with 600 ml of methanol at 20° to give 88.5 g (50 percent) of yellow salt.

A similar reaction using 32.1 g of purified trinitropropyl acetate gave 20.4 g (66 percent) of potassium dinitropropyl acetate. ^1H NMR (D_2O with TMS capillary): δ 2.54 (s, 3H), 3.94 (t, 2H), 4.93 (t, 2H).

2,2-Dinitrobutane-1,4-diol-4-acetate. To a stirred solution of 18.2 g (0.079 mol) of crude potassium 3,3-dinitropropyl acetate in 200 ml of distilled water at ambient temperature was added 19 ml of 36 percent formalin. Concentrated hydrochloric acid (7.3 ml) was added in portions over 10 minutes. At this point there is appreciable oil precipitate and the aqueous phase is only slightly yellow in color (pH approximately 4). After the reaction mixture was stirred for two hours at ambient temperature the oil was extracted into methylene chloride to give 17.3 g (98 percent) of product which was crystallized by cooling a chloroform-hexane solution in dry ice-acetone yielding 13.63 g (78 percent) of white crystals, mp 20-21.5; ^1H NMR (CD_2Cl_2) δ 3.90 (d, 2H), 3.65 (t, 2H), 2.83 (t, 1H), 2.38 (t, 2H), 1.38 (s, 3H).

Analysis calculated for $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_7$: C, 32.44; H, 4.54; N, 12.61. Found: C, 32.40; H, 4.56; N, 12.59.

3,3,7,7-Tetranitro-5-azanonane-1,9-diol-1,9-diacetate. A solution of potassium 3,3-dinitropropyl acetate (87 g, 0.38 mol) in 1050 ml of distilled water and 84 ml of 36 percent formalin was stirred in an ice bath while 45 ml of concentrated hydrochloric acid was added (pH approximately 3). The mixture was heated at 40° for 30 minutes, then cooled to 20° and 42.6 g of ammonium chloride was added. The mixture was stirred vigorously in an ice bath while concentrated ammonium hydroxide solution was added over several hours until the aqueous phase remained yellow and the pH was 5.5-6. At this point an appreciable amount of semisolid had separated from solution and adhered to the walls of the flask. The mixture was stirred overnight before the semisolid was extracted into methylene chloride. Addition of hexane and cooling to 5° gave 58.1 g of white crystals, mp 75-76. The mother liquor was cooled in dry ice-acetone to give a semisolid which was stirred with water and then crystallized from methylene chloride-hexane to give an additional 3.0 g of product, mp 66-70. Total yield (61.1 g) is 76 percent of theoretical. The analytical sample had mp 75.5-76.5°C. ^1H NMR (CDCl_3): δ 2.06 (s, 3H), 2.91 (t, 2H), 3.85 (d, 2H), 4.27 (t, 2H).

Analysis calculated for $C_9H_{14}N_6O_{12}$: C, 33.89; H, 4.50; N, 16.47. Found: C, 33.93; H, 4.62; N, 16.19.

3,3,5,7,7-Pentanitro-5-azanonane-1,9-diol-1,9-diacetate. Acetic anhydride (315 mL) was stirred in an ice bath to maintain a temperature of 20-23° during the slow addition of 95 mL of 90 percent nitric acid. The solution was then cooled to 5° while 3,3,7,7-Tetranitro-5-azanonane-1,9-diol-1,9-diacetate was added in portions with good stirring. The solution was stirred at ambient temperature overnight before it was poured into ice water. The mixture was stirred for one hour and the solid (66.5 g, 97 percent, mp 87-89°C) was removed by filtration. A recrystallized sample (CH_2Cl_2 /hexane) had mp 88-89°C; 1H NMR ($CDCl_3$): δ 2.09 (s, 3H), 3.00 (t, 2H), 4.35 (t, 2H), 5.20 (s, 2H).

3,3,5,7,7-Pentanitro-5-azanonane-1,9-diol(2). Crude pentanitroazanonane-1,9-diol-1,9-diacetate (66.5 g) was stirred in 615 mL of warm (50°C) MeOH in a 2000 mL round-bottom flask. Distilled water (265 mL) was added followed by 19 mL of concentrated hydrochloric acid. The mixture was heated at 67-69°C (mild reflux) overnight before nearly all the solvent was removed under reduced pressure on a rotary evaporator (water bath at 35°). The white solid (mp 118-120°C) was removed by filtration and washed with cold water. Crystallization from methanol-water gave 50.0 g, mp 121.5-123°C. The second crop (2.9 g, mp 118-120°C) raised the yield to 52.9 g (97 percent). 1H NMR (acetone- d_6 + 1 dr. D_2O): δ 3.00 (t, 2H), 2.90 (t, 2H), 5.57 (s, 2H).

Analysis calculated for $C_9H_{14}N_6O_{12}$: C, 24.88; H, 3.65; N, 21.76. Found: C, 24.97; H, 3.70; N, 21.66.

3-Acetoxy-2,2-dinitropropyl Allyl Ether. Heating of 3-hydroxy-2,2-dinitropropyl allyl ether³ (2.06 g, 10.0 mmol) and CH_3COCl (1.57 g, 20.0 mmol) at 60° overnight provided, after removal of volatiles in vacuo, 2.48 g (100 percent) of the liquid title compound; 1H NMR ($CDCl_3$) δ 2.09 (s, 3H), 4.09 (d, J = 5.5 Hz, 2H), 4.32 (s, 2H), 5.01 (s, 2H), 5.30 (m, 2H), 5.80 (m, 1H); mass spectrum m/e (relative intensity) 249 (M+1, 100), 162 (11), 115 (22), 81 (55).

6-Acetoxy-5,5-dinitro-3-oxahexanal. A solution of 3-acetoxy-2,2-dinitropropyl allyl ether (5.00 g, 20.2 mmol) and OsO_4 (0.05 g) in 100 mL of 75 percent dioxane was treated with $NaIO_4$ (9.00 g, 42.0 mmol), in portions, to maintain 26-28° solution temperature.¹² After 1.5 hours the thick suspension of solids was extracted with Et_2O (3x50 mL). Removal of volatiles in vacuo left 5.80 g of crude liquid product composed of a nearly quantitative yield of the aldehyde plus a small amount of dioxane; 1H NMR ($CDCl_3$) δ 2.31 (s, 3H), 4.26 (s, 2H), 4.49 (s, 2H), 5.04 (s, 2H), 9.61 (s, 1H); mass spectrum m/e (relative intensity) 251 (M+1, 100), 232 (8), 206 (57), 204 (18), 191 (48), 159 (15), 146 (30).

6-Acetoxy-5,5-dinitro-3-oxahexanal Oxime. A solution of 6-acetoxy-5,5-dinitro-3-oxahexanal (0.040 mol) and $HONH_2 \cdot HCl$ (0.0425 mol) in 60 mL of 75 percent dioxane was treated with a solution of $NaOOCCH_3$ (0.0425 mol) in 10 mL

³ M. B. Frankel and E. R. Wilson, J. Chem. Eng. Data **26**, 219 (1981).

¹² R. Pappo, D. S. Allen, Jr., R. V. Hemienx, and W. S. Johnson, J. Org. Chem. **21**, 478 (1956).

water and stirred vigorously overnight. Extraction with CH_2Cl_2 (2x100 mL) and removal of volatiles at 50° on a rotary evaporator gave 9.50 g (89 percent) of oxime (E/Z isomer composition of 60/40 by NMR) contaminated with one mol percent dioxane by NMR analysis. An analytical sample was obtained as a light yellow liquid by column chromatography (Silica Gel, CH_2Cl_2): ^1H NMR (CDCl_3) E-isomer δ 2.13 (s, 3H), 4.23 (d, 2H, $J=6\text{Hz}$), 4.42 (s, 2H), 5.03 (s, 2H), 7.50 (t, 1H, $J=6\text{Hz}$); Z-isomer 2.13 (s, 3H), 4.46 (s, 2H), 4.51 (d, 2H, $J=3\text{Hz}$), 5.03 (s, 2H), 6.90 (t, 1H, $J=3\text{Hz}$), mass spectrum m/e (relative intensity) 266 (M+1, 100).

Analysis calculated for $\text{C}_2\text{H}_{11}\text{N}_3\text{O}_8$: C, 31.70; H, 4.18; N, 15.85. Found: C, 31.56; H, 4.31; N, 15.68.

7-Acetoxy-1-fluoro-1,1,6,6-tetranitro-4-oxa-2-heptanol. A mixture of $\text{CF}(\text{NO}_2)_2\text{H}$ (10.0 mmol) and the 6-acetoxy-5,5-dinitro-3-oxahexanal (8.4 mmol) in 60 mL of 65 percent CH_3OH was treated with NaHCO_3 in portions (total of 0.62 g) to maintain pH 5.5-6.0.

The solution was acidified after 3.5 hours and extracted with CH_2Cl_2 (3x50 mL). Concentration in vacuo of the dried (MgSO_4) CH_2Cl_2 solution gave 2.77 g of crude liquid product. Crystals (mp $76-80^\circ$, 1.32 g (42 percent)) were obtained from CH_2Cl_2 -hexane. Further recrystallization provided an analytical sample of the title compound with mp $84-85^\circ$; ^1H NMR (CDCl_3) δ 2.11 (s, 3H), 3.85 (d, 2H, $J=4\text{ Hz}$), 4.34 (s, 2H), 4.91 (s, 2H), 5.18 (d of t, ^3H , $J_{\text{CH}_2-\text{CH}}=4\text{ Hz}$, $J_{\text{CH}-\text{CF}}=18\text{ Hz}$).

Analysis calculated for $\text{C}_8\text{H}_{11}\text{FN}_4\text{O}_{12}$: C, 25.68; H, 2.96; F, 5.08; N, 14.97. Found: C, 25.75; H, 2.93; F, 4.96; N, 14.85.

1-Fluoro-1,1,6,6-tetranitro-4-oxa-2,7-heptanediol (3). Stirring 0.50 g of the above acetate with 10.0 g concentrated H_2SO_4 for two hours gave, after drowning on ice and Et_2O extraction, 0.48 g of diol contaminated with acetic acid. Storage over KOH pellets at 0.1 mm gave 0.41 g (92 percent) of diol 3 as a light yellow liquid; ^1H NMR (CDCl_3) δ 2.7 (broad s, 2H), 3.91 (d, 2H, $J=4\text{ Hz}$), 4.44 (s, 4H), 5.22 (d of t, 1H, $J_{\text{CH}_2-\text{CH}}=4\text{ Hz}$, $J_{\text{CH}-\text{CF}}=9\text{ Hz}$).

7-Acetoxy-2,2,6,6-tetranitro-4-oxaheptanol. A solution of 10.0 g (37.7 mmol) of 6-acetoxy-5,5-dinitro-3-oxahexanal oxime in 100 mL CH_2Cl_2 at 5° was treated dropwise over 0.75 hours with 18.8 mL of 90 percent HNO_3 .¹³ An ice/MeOH bath was used to maintain $5-8^\circ$ solution temperature throughout the addition and especially to control an exotherm which occurs during the first part of the addition and which is accompanied by a transient blue color and evolution of brown fumes. The brown solution was further treated at $5-8^\circ$ with 12.2 mL of 30 percent H_2O_2 and then poured on ice. The dried (Na_2SO_4) CH_2Cl_2 layer was concentrated to 9.39 g of light red liquid in vacuo. NMR analysis of a 0.4 g aliquot in CDCl_3 with 100 mg of $\text{HCCl}_2\text{CCl}_2\text{H}$ as internal standard indicated the presence of 10.7 mmol (28 percent) of $\text{AcOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{H}$ as a triplet, $\text{C}(\text{NO}_2)_2\text{H}$, ($J=5.8\text{Hz}$) at δ 6.57 and 1.8 mmol (5 percent) of 6-acetoxy-5,5-dinitro-3-oxahexanal as a singlet, CHO, at δ 9.68. The remainder of the red product

¹³ V. Grakauskas, J. Org. Chem. 38, 2999 (1978).

mixture (9 g) was mixed with 2.5 g (30 mmol) of a 36 percent formalin solution in 50 ml of 75 percent dioxane (pH 2). After three hours the solution was further acidified with 6M HCl and extracted with CH₂Cl₂ (2x50 ml). This solution was stirred overnight with an equal volume of 25 percent NaHSO₃ and then concentrated in vacuo to a liquid residue which was chromatographed on silica gel (55 g) with CH₂Cl₂/hexane (75/25) followed by CH₂Cl₂ and CH₂Cl₂/E+OAc (95/5). This provided 2.23 g (17 percent based on starting oxime) of pure title compound plus an additional 0.90 g of slightly impure product: ¹H NMR (CDCl₃) δ 2.16 (s, 3H), 4.53 (s, 4H), 4.59 (s, 2H), 5.01 (s, 2H); mass spectrum m/e (relative intensity) 357 (M+1, 80), 327 (18), 310 (7), 252 (33), 222 (14), 209 (12), 119 (100), 104 (48), 86 (34).

3-Hydroxy-2,2-dinitropropyl Ether (4). A mixture of 2.42 g of the above acetate and 20 ml concentrated H₂SO₄ was stirred for two hours and poured on ice to give 200 ml of homogeneous solution. Saturation with NaCl and extraction with E+2O (5x200 ml) gave 2.21 g of crude product, which after storage over P₂O₅ at 0.1 mm for several days gave 1.65 g (77 percent) of the diol 4 which had partially crystallized; ¹H NMR ((CD₃)₂CO) δ 4.49 (s, 4H), 4.74 (s, 4H); mass spectrum m/e (relative intensity) 315 (M+1, 52), 285 (24), 255 (8), 208 (3), 167 (65), 149 (20), 137 (24), 119 (100).

3,3,3-Fluorodinitro-1,2-propanediol.⁵ 2,2-Diethoxy-ethanol, 13.4 g, was dissolved in 50 ml water, 1 ml 2N H₂SO₄ was added and the mixture stirred approximately one hour at 50°C. After cooling in an ice-bath, 12.4 g fluorodinitromethane was added with stirring followed by sufficient NaHCO₃ solution to give a pH of 6. The fluorodinitromethane slowly dissolved. After stirring for an additional hour with ice cooling, the mixture was acidified (H₂SO₄), saturated with NaCl, and extracted with ether. The extract was dried (MgSO₄) and freed from solvent to give the crude product as a pale yellow oil; ¹H NMR (CDCl₃) δ 2.58 (s, 2H), 3.97 (d, 2H), 5.16 (double t, 1H).

4,4,4-Trinitrobutyraldoxime. 3,3,3-Trinitrobutyraldehyde,¹⁴ 7.3 g (35 mmol), was dissolved in 60 ml 75 percent dioxane; a solution of 2.8 g (40 mmol) NH₂OH·HCl and 5.45 g (40 mmol) NaOAc·3H₂O in 9 ml water was added and the mixture stirred at room temperature for 6-8 hours. After dilution to 300 ml with water the mixture was extracted with 2x100 ml CH₂Cl₂, the extract dried (MgSO₄) and freed from solvent at ambient temperature in vacuo. The remaining oil is a mixture of cis and trans oxime contaminated by dioxane if solvent removal was incomplete. ¹H NMR (CDCl₃): δ approximately 2.55 (m), 3.15 (m), 6.60 (t), 7.29 (t).

Attempted Preparation of 1,1,1,4,4-Pentanitro-butane (6). Several variations of the procedure of Grakauskas¹³ for the nitration/oxidation of fluorodinitro-acetaldoxime were tried. Variations included temperature, HNO₃ concentration (90 percent, 100 percent), normal/reverse addition, addition of NH₄NO₃ to the HNO₃. Only a transient blue color was observed in most cases, in some no blue color at all. All of the products obtained on work-up were yellow oils which were mainly mixtures of trinitrobutyraldehyde and a second component which is

⁵ L. T. Eremenko and F. V. Oreshko, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 1765.

¹⁴ D. L. Ross, C. L. Coon, M. E. Hill, and R. L. Simon, *J. Chem. Eng. Data*, **13**, 437 (1968).

¹³ V. Grakauskas, *J. Org. Chem.* **38**, 2999 (1978).

believed to be the pentanitrobutane on the basis of the NMR data, primarily the presence of a triplet at δ 5.4 (CDCl_3) which disappeared on addition of D_2O and is indicative of $\text{CH}_2\text{C}(\text{NO}_2)_2\text{H}$. The ratio of the two components can be estimated from the ratio of this triplet and the CHO singlet at δ 9.75. No attempts to isolate 6 were made.

5,5-Dinitro-1,3-dioxepane (7). A solution of 1.0 g 1 in 15 ml warm CH_2Cl_2 was added with ice cooling to a solution of 0.2 g paraformaldehyde in 6 ml 90 percent H_2SO_4 . After two hours stirring at room temperature, the mixture was poured onto crushed ice and the product extracted with CH_2Cl_2 . After drying (MgSO_4) and removal of solvent, 0.75 g (70 percent) 7 was obtained as a colorless oil of excellent purity (GC, NMR); ^1H NMR (CDCl_3): δ 2.81 (t, 2H), 4.07 (t, 2H), 4.75 (s, 2H), 4.83 (s, 2H).

4-Fluorodinitromethyl-1,3-dioxolane. To a solution of 0.9 g paraformaldehyde in 6 ml concentrated H_2SO_4 was added with ice-cooling 5.52 g 3,3,3-fluorodinitro-1,2-propanediol. The mixture was stirred six hours at room temperature and then poured on ice. The product was extracted with CH_2Cl_2 and the extract washed twice with 0.02 N NaOH, dried (MgSO_4) and freed from solvent to give 3.6 g of an oil which was distilled at about 1 Torr (bp 45-50°C) to give the pure product. ^1H NMR (CDCl_3): δ 4.35 (m, 2H), 5.13 (d, 2H), 5.37 (m, 1H).

Analysis calculated for $\text{C}_4\text{H}_5\text{FN}_2\text{O}_6$: C, 24.50; H, 2.57; N, 14.28; F, 9.69. Found: 24.51; H, 2.62; N, 14.47; F, 11.10.

Reaction of 3 with $\text{CH}_2\text{O}/\text{H}_2\text{SO}_4$. A 0.93 g (2.8 mmol) sample of 3 in 5 ml CH_2Cl_2 was exposed to 0.093 g (3.1 mmol) of paraformaldehyde in 6 ml of 96 percent H_2SO_4 for 16 hours at 20° without effect as ascertained by TLC and IR analyses of recovered diol (Et_2O extraction of drowned reaction mixture). Recovered 3 mixed with paraformaldehyde in 90 percent H_2SO_4 (three ml) and four ml CH_2Cl_2 for 18 hours at 20° gave similar results. Recovered 3 from this reaction was finally mixed with paraformaldehyde in 100 percent H_2SO_4 (three ml) and four ml CH_2Cl_2 for 17 hours at 20°. Small amounts of products were indicated by TLC and GPC analyses (see the discussion on page 6); in addition, 76 percent of 3 was recovered.

Reaction of 4 with $\text{CH}_2\text{O}/\text{H}_2\text{SO}_4$. Diol 4 (0.830 g, 2.64 mmol) in a solution of 2.4 ml 96 percent H_2SO_4 and 1.2 ml sulfolane was reacted with 0.071 g (2.4 mmol) trioxane at 20° for two hours. The solution became cloudy after 0.3 hours. It was quenched on 25 g ice and this solution filtered to give 0.055 g of white solid. Extraction of the aqueous solution with 10 ml Et_2O gave 0.218 g of yellow liquid. The solid was homogeneous by GPC analysis but had a broad melting range (159-170°C with solid still present). ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 4.73 (s, 4H), 4.87 (s, 4H), 4.97 (s, 2H), consistent with structure 8. GPC analysis of the liquid product showed four peaks arrayed in the shape of a 1:3:3:1 quartet (RI detection) with the third peak corresponding in retention time to the solid product above. Sulfolane was present as a contaminant.

Reaction of 5 with $\text{CH}_2\text{O}/\text{H}_2\text{SO}_4$. The reaction components, 90 percent or concentrated sulfuric acid, sulfolane, diol 5, and trioxane were mixed in several different ways: (1) diol, 1g, was dissolved in a mixture of 3 ml H_2SO_4 and 1-2 ml sulfolane, if necessary with slight warming; trioxane, 0.1 g, was added as a methylene chloride solution; the methylene chloride was removed by entraining in a stream of nitrogen; (2) diol was added to a solution of the trioxane in H_2SO_4 /sulfolane. After a reaction time of two hours, the mixture was poured on ice, stirred, the solid filtered off and digested with 25 ml hot water and filtered again. Yields ranged from 0.85 to 1.0 g. The products were analyzed by GPC on a 80 cm Varian Micropac TSK 3000H column, pore size 1500 Å, THF solvent, flow rate 0.5 ml/minute. UV analysis was carried out by dissolving the diol in THF and diluting into a mixture of THF, water, and NaOH such that the final solution was 0.01 n in NaOH and contained 50 percent water (v/v).

Attempted Mannich Reactions of 1,3-Diamino-2-propanols with Nitromethane. Mannich reactions of 1,3-diamino-2-propanol with formaldehyde and nitromethane (1:5:1 mol ratio) to form a hydroxynitrodiazocine were attempted in water and in CH_3OH solvents with the amine and its acetate salt. Conditions ranged from room temperature to reflux, in the case of CH_3OH as solvent. The major products in all cases had very low RF on TLC analysis under conditions where the desired product would be expected to have eluted without difficulty. The product mixtures were generally dark in color and of a gummy consistency. Similar results were obtained with 1,3-di-*t*-butylamino-2-propanol¹⁵ and its salts (hydrochloride and acetate) in water and in CH_3OH under conditions ranging from 24 hours at 20° to 65 hours reflux, in the case of CH_3OH solvent. These experiments also included anhydrous conditions in CH_3OH with the use of para-formaldehyde rather than formalin.

Attempted Oxidation of 3,7-Dihydroxy-1,5-octahydrodiazocines. The 1,5-di-*t*-butyl and the 1,5-ditosyl derivatives were prepared by literature procedures¹⁶ and were oxidized under a variety of conditions including pyridinium dichromate, Jones reagent and chromic acid; these led only to hemiketal formation as had been observed previously.¹⁵

1-*i*-Propyl-3,3,7,7-tetranitro-5-nitroso-1,5-octahydrodiazocine (10b). To 0.5 g bis(dinitroethyl) nitrosamine was added 4.5 ml 60 percent aqueous MeOH and 0.23 g AcOH (glacial). To this, at 15-20°C, was added 1.1 ml 20 percent aqueous *i*-PrNH₂ (0.21 g *i*-PrNH₂) and 0.6 ml aqueous formaldehyde (37 percent). The pH was adjusted to 3.5-4.0 with AcOH and the mixture was heated at 30°C for three hours. The solid was filtered off and washed with H₂O, keeping the washings separate from the filtrate. The filtrate was stirred at 30°C overnight. The solid was filtered off, washed with H₂O and dried to give a total of 0.29 g (47 percent); mp 123-4°C (from CH_2Cl_2 /hexane); ¹H NMR (CDCl_3): δ 0.90 (d, 6H), 2.70 (m, 1H), 3.43 (s, 2H), 3.83 (s, 2H), 5.00 (s, 2H), 5.88 (s, 2H).

¹⁵ V. R. Gaertner, Tetrahedron **23**, 2123 (1967).

¹⁶ W. W. Pandler, G. R. Gapski, and J. M. Barton, J. Org. Chem. **31**, 277 (1966).

Analysis calculated for $C_9H_{15}N_2O_9$: C, 29.60; H, 4.14; N, 26.84. Found: C, 29.80; H, 4.28; N, 26.71.

3,3,7,7-Tetranitro-1-nitroso-1,5-octahydrodiazocine (10c). To 14.0 g bis(dinitroethyl)nitrosamine was added 126 ml 60 percent aqueous MeOH and 6.4 g HOAc (glacial). To this was then added, at 15-20°C, 12.9 ml NH_3 (aqueous) in 13 ml H_2O followed by 16.8 ml aqueous formaldehyde (37 percent). The pH was then adjusted to four with HOAc. Solid started forming as the pH was being adjusted. The mixture was stirred overnight at room temperature. The solid was then filtered off, washed with H_2O and dried in a vacuum desiccator to give 13.8 g (81 percent) 10c; mp 159.5-160.5°C (dec.) (from CH_2Cl_2 /hexane). 1H NMR ($CDCl_3$ /acetone- d_6) δ 3.0-3.3 (1H), 3.60 (d, 2H), 4.10 (d, 2H), 4.97 (s, 2H), 5.83 (s, 2H).

Analysis calculated for $C_6H_9N_7O_9$: C, 22.30; H, 2.81; N, 30.34. Found: C, 22.26; H, 2.85; N, 30.54.

1,3,3,5,7,7-Hexanitro-1,5-octahydrodiazocine (9). To 100 ml concentrated H_2SO_4 at 0-5°C in an ice bath was added 7.5 g 3,3,7,7-tetranitro-1-nitroso-1,5-octahydrodiazocine (10c). To this was added a mixture of 23.5 ml 90 percent HNO_3 and 41.2 ml concentrated H_2SO_4 over a period of two hours. The mixture was then poured onto ice. The solid was filtered off, washed with H_2O and dried under vacuum to give 6.8 g (76 percent) of product which can be recrystallized from CH_3CN or CH_3NO_2 ; mp approximately 250°C (dec.); 1H NMR (acetone d_6) δ 5.70 (s).

A smaller scale run in which the total reaction time was less gave a considerably better yield (90 percent).

Analysis calculated for $C_6H_8N_8O_{12}$: C, 18.75; H, 2.08; N, 29.17. Found: C, 19.07; H, 2.07; N, 28.96.

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Appendix A

Nitrolysis of Dialkyl *tert*-Butylamines

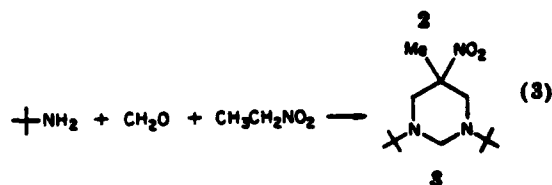
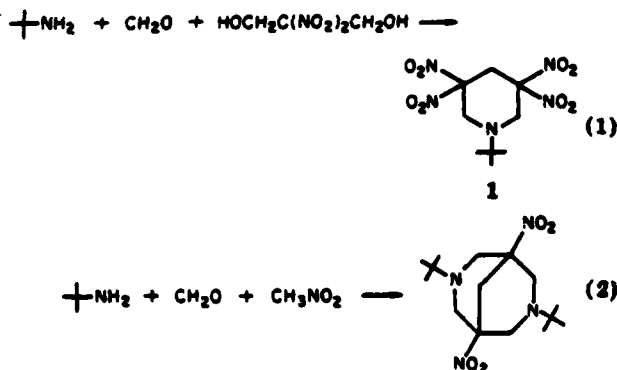
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Received December 28, 1981

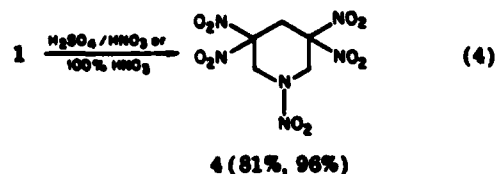
In the synthesis of secondary nitramines, especially cyclic ones, an N-blocking group is often required to control the course of Mannich condensations; the N substituent is subsequently removed by nitrolysis to give the nitramine. *N*-Acyl and *N*-alkyl groups have been used for this purpose with varying success.¹⁻⁶ Earlier work in our laboratory on *N*-*tert*-butyl-2,2,2-fluorodinitroethanamides⁶ and -amines⁷ suggested that the *tert*-butyl group might be particularly useful in this regard. We now report on the nitrolysis of *N*-*tert*-butylamines containing (mostly nitroalkyl) substituents of varying electron demand.

The amines 1-3 used as model compounds in the present work were obtained by the Mannich condensation of *tert*-butylamine with the appropriate nitroalkanes (eq 1-3),



largely analogous to reported syntheses of similar tertiary and secondary amines.⁸ The synthesis of 2 illustrates the utility of the N-blocking group since with ammonia 7-nitro-1,3,5-triazaadamantane is obtained.⁹

The facile conversion of *tert*-butylbis(2,2,2-fluorodinitroethyl)amine to bis(2,2,2-fluorodinitroethyl)amine in concentrated sulfuric acid⁷ and the ability of mixed acid ($\text{H}_2\text{SO}_4/\text{HNO}_3$) to nitrate the latter¹⁰ indicated that bis-(2,2-dinitroalkyl)-substituted *tert*-butylamines should be nitrolyzed readily by mixed acid. This was shown to be the case for 1 which was converted to 4 in excellent yield with either mixed or 100% nitric acids (eq 4).



For substrates with fewer β -nitro groups the situation is more complex. In some cases complete or partial nitrolysis occurred in mixed acid; some substrates were unreactive toward this reagent, but could be nitrolyzed with acetic anhydride/nitric acid or with 100% nitric acid alone. Thus, the diazine 5 was nitrolyzed quickly to 6 (eq 5) in

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(3) J. H. Robson and J. Reinhardt, *J. Am. Chem. Soc.*, **77**, 107, 2463 (1955); see also ref 1 and 2.

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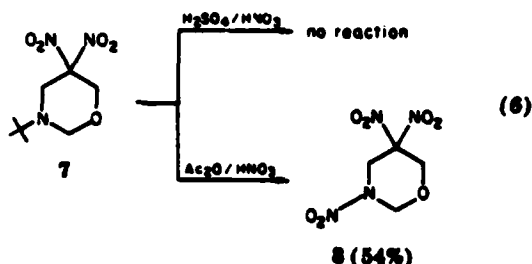
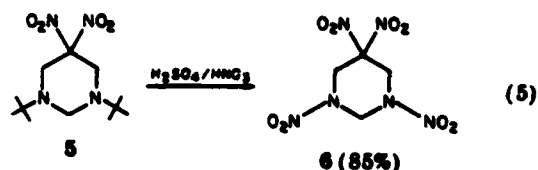
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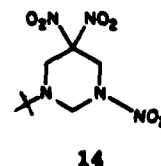
nitrodiamines 2 and 3. Nitrolysis in mixed acid caused the displacement of only one *tert*-butyl group, whereas with 100% HNO_3 , both *tert*-butyl groups were nitrolyzed (eq 7 and 8).

tert-Butyldimethylamine was studied as an example devoid of any nitro substituents. With mixed acid and with 90% or 100% HNO_3 , no or only trace amounts of nitramines were produced. With nitric acid/acetic anhydride, dimethylnitramine was formed in about 15% yield. TLC analysis of the reaction mixture indicated that *tert*-butylmethylnitrosamine was also present; dimethylnitrosamine, however, was not formed. A higher yield of mixed acid at room temperature. The analogous oxazine 7, however, was unreactive under the same conditions (except that decomposition occurred on extended exposure) but was nitrolyzed with the milder reagent $\text{Ac}_2\text{O}/\text{HNO}_3$ (eq 6). Similarly peculiar was the behavior of the

dimethylnitramine, 55%, was obtained by using the amine hydrochloride for nitrolysis. As in the nitration of secondary amines,² chloride ion appears to have a catalytic effect in the nitrolysis of the tertiary amine also.

The results obtained have thus confirmed the expectation that dialkyl *tert*-butylamines can be nitrolyzed readily to the corresponding dialkylnitramines. The nitrolyses occur in preparatively useful yields ranging from 55% to 85% for a variety of nitro-substituted and unsubstituted amines. Improvement of the yields may be possible since attempts at their optimization were generally not made.

A possible explanation of the differing behavior of substrates 2, 3, 5, and 7 toward the three nitrolysis agents used here may be based on differences in the basicities of the nitrogens. Effects of basicity on the nitration of secondary amines² and the nitrolysis of hexamine and other methylenediamines,¹¹ of the *N*-alkyl group in 2,4-dinitroanilines,² and of 1-alkyl-3,6-dinitroperhydro-1,3,6-triazepines⁴ have been previously noted. The lack of reactivity of 7, 9, and 13 in mixed acid may thus be due to their complete protonation at the *tert*-butyl nitrogens in this medium which would prevent attack by NO_2^+ or a similar nitrating species. In the less acidic media, 100% HNO_3 , and acetic anhydride/nitric acid, a larger amount of unprotonated substrate may be present, and nitrolysis proceeds. The diamines 2, 3, and 5 may be largely mono-protonated in mixed acid, thereby leaving the second N vulnerable to attack by NO_2^+ . Even the fact that 14, which



must be an intermediate in the mixed-acid nitrolysis of 5 to 6, undergoes further nitrolysis in that medium while 9

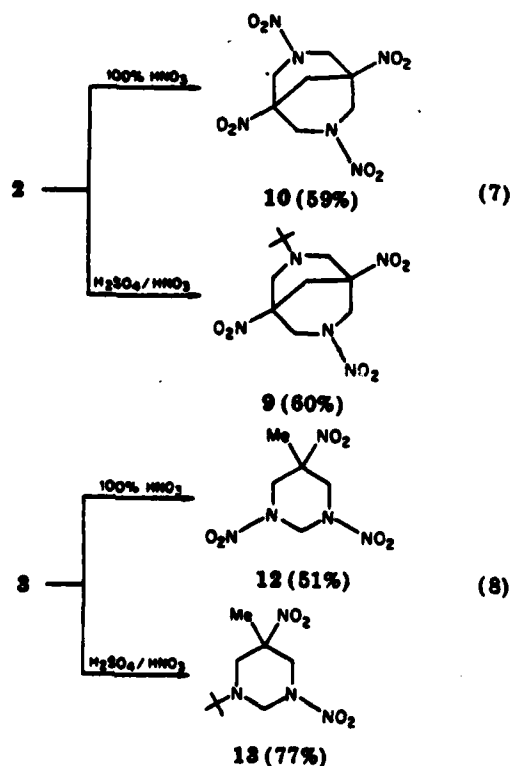


Table I. Properties and Analyses of Nitrolysis Products^a

compd	mp, °C	¹ H NMR, δ
6	153-154	6.13 (s, NCH ₃ N), ^c 5.23 (s, CCH ₃ N)
8	88-89	4.68 (s, 2 H), ^b 5.18 (s, 2 H), 5.45 (s, 2 H)
10	273-274 dec	3.30 (s, CCH ₃ C), ^c 4.24 (d, NCHC), 5.39 (d, NCHC)
9	93-94	1.03 (s, 9 H), ^c 2.67 (d, 2 H), 2.81 (m, 2 H), 3.64 (d, 2 H), 3.81 (d, 2 H), 5.40 (d, 2 H)
12	167-168	1.80 (s, 3 H), ^c 4.12 (d, 2 H), 5.18 (d, 1 H), 5.41 (d, 2 H), 7.05 (d, 1 H)
13	100.5-102	1.12 (s, 9 H), ^b 1.56 (s, 3 H), 2.67 (d, 1 H), 3.63 (d, 1 H), 3.72 (d, 1 H), 4.11 (d, 1 H), 5.02-5.21 (m, 2 H)

^a CDCl_3 /1 drop of $\text{Me}_2\text{SO}-d_6$. ^b CD_2Cl_2 . ^c Acetone- d_6 .

^d Satisfactory analytical values ($\pm 0.3\%$ for C, H, and N) were reported for all compounds in this table.

and 13 do not can be rationalized on the basis of differences in the basicities of the remaining *tert*-butyl nitrogens.

(11) P. A. S. Smith, "Open Chain Nitrogen Compounds", Vol. II, W. A. Benjamin, New York 1966, p 504.

Experimental Section

Caution: Several of the compounds reported herein, especially 4, 6, 8, and 10, are sensitive explosives and should be handled with appropriate care. Elemental analyses were obtained commercially. ¹H NMR spectra are from various sources; chemical shifts are given in parts per million from Me₄Si.

1-*tert*-Butyl-3,3,5,5-tetranitropiperidine (1). Glacial AcOH was added to 1 mL of *tert*-butylamine in 15 mL of H₂O to a pH of 6, followed by addition of 1.6 g 2,2-dinitro-1,3-propanediol. During 6 days of stirring the mixture at room temperature the pH was adjusted periodically to 6 as necessary with AcOH or NaOAc. The crude product was filtered off; extraction of the filtrate with CH₂Cl₂ and washing of the extract with H₂O gave an additional crop: total yield 0.25 g (15%); mp 136–137 °C (from MeOH/H₂O); ¹H NMR (CD₂Cl₂) δ 1.16 (s, CH₃), 3.71 (s, CCH₂C), 4.03 (s, CCH₂C).

Anal. Calcd for C₉H₁₅N₅O₈: C, 33.65; H, 4.71; N, 21.80. Found: C, 33.61; H, 4.73; N, 21.88.

3,7-Di-*tert*-butyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonane (2). To an ice-cooled solution of 36.5 g of *tert*-butylamine in 150 mL of MeOH was added 30 g of AcOH with stirring, followed by 20.4 g of nitromethane and 30.0 g of paraformaldehyde. The mixture was heated to a mild reflux for 4 days, kept at ca. -10 °C overnight, and filtered. The dark brown solid was triturated with 100 mL of a pH 6 buffer solution to give 7.2 g of crude product which was purified by a combination of chromatography on silica gel (CH₂Cl₂) and recrystallization from MeOH. Additional product can be obtained by adding the initial filtrate to 1500 mL of H₂O, stirring several h, filtering off the solid, and chromatographing it on silica gel (CH₂Cl₂). The initial solid fractions were combined and purified as above. The pH 6 buffer wash was made basic and extracted with CH₂Cl₂ and the extract was washed with H₂O, and dried. Chromatography and recrystallization as above gave a further crop of product: total yield 3.7 g (7%); mp 135–136 °C; ¹H NMR (CDCl₃) δ 1.11 (s, CH₃), 2.64 (s, CCH₂C), 3.01 (AB q, NCH₂C).

Anal. Calcd for C₁₉H₂₉N₅O₄: C, 54.86; H, 8.59; N, 17.06. Found: C, 55.07; H, 8.59; N, 17.09.

1,3-Di-*tert*-butyl-5-methyl-5-nitrohexahydro-1,3-diazine (3). To 1.5 g of nitroethane in 10 mL of MeOH were added 4 mL of 36% formaldehyde solution and 2 mL of *tert*-butylamine, and the mixture was stirred overnight and cooled to ca. -10 °C. The solid was filtered, washed with H₂O, and recrystallized from MeOH/H₂O. The initial crop was a mixture, the second crop afforded 0.2 g of 3, mp 106–109 °C. Additional material can be obtained by fractional crystallization of the initial crop: ¹H NMR (CD₂Cl₂) δ 1.08 (s, 18 H), 1.46 (s, 3 H), 2.31 (d, 2 H), 2.88 (d, 2 H), 3.59 (d, 2 H), 3.85 (d, 1 H).

Anal. Calcd for C₁₃H₂₇N₃O₂: C, 60.67; H, 10.58; N, 16.33. Found: C, 60.59; H, 10.63; N, 16.22.

Nitrolysis. The nitrolyses were carried out by three general methods. Properties and analytical data for new products are listed in Table I.

Method A. The dialkyl *tert*-butylamine was added to concentrated H₂SO₄ with cooling in ice. To this mixture was added at 0 °C a mixture of 90% HNO₃ and concentrated H₂SO₄. After being stirred, the solution was poured onto ice and the product isolated as described below.

Method B. The dialkyl *tert*-butylamine was added to 100% HNO₃ at 0 °C under N₂. After being stirred, the solution was poured onto ice and the product isolated as described below.

Method C. To acetic anhydride under N₂ was added 100% HNO₃, keeping the temperature below 20 °C. To this solution at 5–10 °C was added the dialkyl *tert*-butylamine in AcOH. After being stirred, the solution was poured onto ice and the product isolated as described below.

1,3,3,5,5-Pentanitropiperidine (4). Method A, with 0.2 g of 1 in 3 mL of H₂SO₄ and a mixture of 0.8 mL of HNO₃ and 1.3 mL of H₂SO₄ and after overnight stirring at room temperature, filtering off of the solid, washing with water, and recrystallization (CH₂Cl₂/hexane), gave 0.15 g (81%) of 4. Method B, with 0.1 g of 1 and 2 mL of HNO₃ and after 3 days at room temperature, filtering off of the solid, extraction of the filtrate (CH₂Cl₂), and purification of the product as in method A, gave 0.09 g (96%) of 4. The products were identical by melting point and IR with an authentic sample.

1,3,5,5-Tetranitrohexahydro-1,3-diazine (6). Method A, with 7.5 g of 5 in 100 mL of H₂SO₄ and a mixture of 17 mL of HNO₃ and 27 mL of H₂SO₄ and after 1 h at 0 °C and 2 h at room temperature, extraction (CH₂Cl₂), drying (MgSO₄), concentration, addition of hexane, and cooling, gave 6.05 g (87%) of 6.

3,5,5-Trinitrotetrahydro-1,3-oxazine (8). Method C, with 2 mL of Ac₂O, 0.8 mL of HNO₃ and 1.0 g of 7 in 2 mL of AcOH and after warming of the mixture to room temperature over 4 h and overnight stirring at room temperature, extraction (CH₂Cl₂), washing with H₂O, and purification by recrystallization (CH₂Cl₂/hexane), gave 0.56 g (54%) of 8.

1,3,5,7-Tetranitro-3,7-diazabicyclo[3.3.1]nonane (10). Method B, with 0.2 g of 2 and 2.0 mL of HNO₃ and after 0.5 h at 0 °C and 3 days at room temperature, filtering off of the solid, extraction of the filtrate (CH₂Cl₂), washing of the extract with dilute K₂CO₃ solution and H₂O, and recrystallization (CH₂Cl₂/hexane) of the combined product, gave 0.11 g (59%) of 10.

7-*tert*-Butyl-1,3,5-trinitro-3,7-diazabicyclo[3.3.1]nonane (9). Method A, with 0.1 g of 2 in 2.5 mL of H₂SO₄ and a mixture of 0.6 mL of HNO₃ and 1 mL of H₂SO₄ and after 1 h at 0 °C and 1 h at room temperature, extraction (CH₂Cl₂), washing with dilute K₂CO₃ solution and H₂O, and recrystallization (MeOH/H₂O), gave 0.06 g (62%) of 9.

1-*tert*-Butyl-3,5-dinitro-5-methyl-1,3-hexahydrodiazine (13). Method A, with 0.1 g of 3 in 2.5 mL of H₂SO₄ and a mixture of 0.6 mL of HNO₃ and 1.0 mL of H₂SO₄ and after 15 min at 0 °C, extraction (CH₂Cl₂), washing with H₂O, and recrystallization of the crude product (MeOH/H₂O), gave 0.07 g (77%) of 13.

5-Methyl-1,3,5-trinitrohexahydro-1,3-diazine (12). Method B, with 5 mL of HNO₃ and 0.1 g of 3 and after 15 min at 0 °C and 6 h at 35–45 °C, filtering off the solid, and recrystallization (CH₂Cl₂/hexane), gave 0.043 g (51%) of 12.

Nitrolysis of *tert*-Butyldimethylamine. To 10 mL of Ac₂O at 0–5 °C was added 2.9 mL of oxide-free 90% HNO₃, followed by a solution of 1.0 g of *tert*-butyldimethylamine in 3.0 mL of AcOH. The mixture was stirred 2 days at room temperature and poured onto ice. After the mixture was stirred 2 h, the product was extracted (CH₂Cl₂). The aqueous phase was made basic (Na₂CO₃) and extracted again (CH₂Cl₂). The combined extracts were washed (dilute NaHCO₃), dried (MgSO₄), and concentrated by distillation. Addition of hexane and chilling gave 0.143 g (16%) of dimethylnitramine. Further concentration gave no additional product.

Nitrolysis of *tert*-Butyldimethylamine Hydrochloride. The same procedure as above was used with 11.5 mL of Ac₂O, 2.5 mL of oxide-free HNO₃, and a solution of 2.0 g of the amine hydrochloride in 2 mL of AcOH. A workup as above gave 0.51 g of dimethylnitramine as a first crop. Further concentration gave another 0.21 g (total yield 54%).

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methane, 75-52-5; nitro ethane, 79-24-3; *tert*-butyldimethylamine, 918-02-5; dimethylnitramine, 4164-28-7; *tert*-butyldimethylamine hydrochloride, 6338-78-9.

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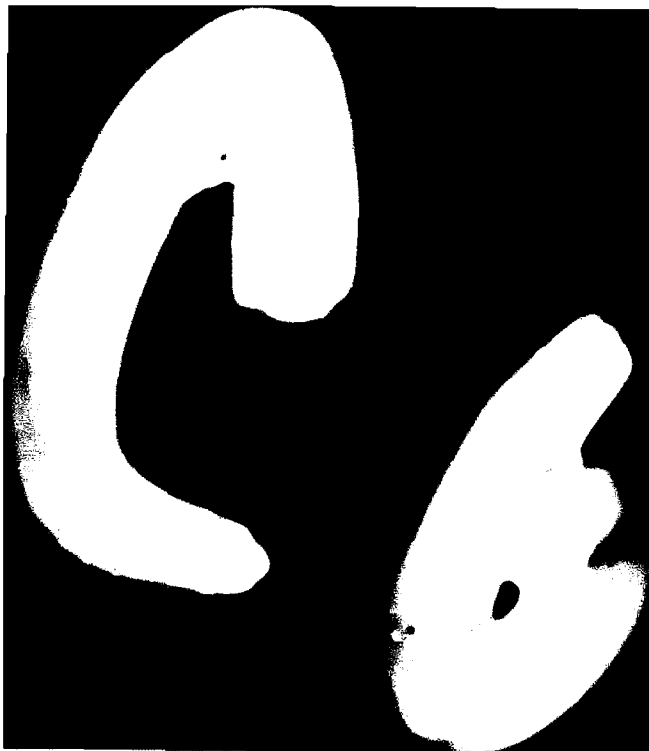
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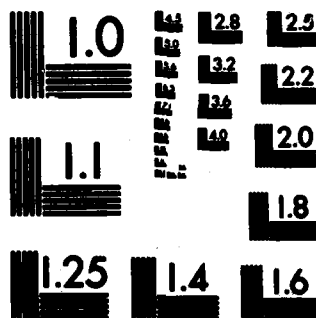
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Page 22, line 16, change 2,2-Dinitropropanol to 3,3-Dinitropropanol

Page 22, line 12 from the bottom, change 2.95 to 3.95

Page 23, lines 20 and 21 from the bottom, add 0.68 to all NMR
chemical shifts; the correct shifts are: 4.58, 4.33,
3.51, 3.06, 2.06

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